UNIVERSITÉ DE MONTPELLIER

T H È S E

Pour obtenir le grade de
DOCTEUR DE L'UNIVERSITE DE MONTPELLIER
Spécialité : Mécanique et Génie Civil
Ecole Doctorale : Information, Structures, Systèmes

Associations tanins-bore pour des produits de protection du bois à faible impact environnemental

Par
Jinbo HU

Soutenance prévue le 01 Septembre 2015

JURY

Bertrand CHARRIER	(Université de Pau et des Pays l'Adour)	Rapporteur
Pierre-Jean MEAUSOONE	(Université de Lorraine)	Rapporteur
Joseph GRIL	(Université de Montpellier)	Examinateur
Yiqiang WU	(Université du Centre-Sud de la science et de la technologie (Chine))	Examinateur
Gianluca TONDI	(Université de Salzbourg (Autriche))	Invité
Marie-France THEVENON	(CIRAD, Montpellier)	Directrice de Thèse

Acknowledgement

First and foremost I would like to thank my PhD advisors, Dr. Marie-France Thevenon, Prof. Tony Pizzi and Dr. Gianluca Tondi, for supporting me during these past three years. I especially want to thank Marie-France for providing me with the opportunity to complete my PhD thesis in Cirad. She always made time to discuss my work and result issues. Her warm encouragement and thoughtful guidance made my thesis work possible. Prof. Pizzi has been supportive and has given me the freedom to pursue various issues without objection. He has also provided insightful discussions about the research. I am also very grateful to Gianluca for his patience, enthusiasm, and guidance in my work and many insightful discussions and suggestions.

I would also like to thank my committee members, Prof. Charrier, Prof. Meausoone, Prof. Gril and Prof. Wu for serving as my committee members.

I wish to express my sicere thanks to BioWooEB (Unit of Biomass, Wood, Energy, Bioproducts), principal of the laboratory prepared the thesis, for providing me with all the necessary facilities for the research. To all my colleagues from BioWooEB in CIRAD, many thanks for their kindnesses and all their helps are placed on record.

I thank the colleagues from Forest Product Technology & Timber Construction Department in Salzburg University of Applied Sciences (Austria) who provided insight and expertise that greatly assisted the research.

I would also like to thank Dr. Ormondroyd and Mr. Skinner for being a friendly host and allowing me to perform research work of LCA in their laboratory at Bangor university (UK) and for being available at all times for discussions. Thanks also go to the colleagues at BioComposites Centre for providing an enjoyable place to work in.

I would like to thanks the Wood team (Equipe Bois) at laboratory of LMGC (Laboratoire de Mécanique et Génie Civil), where has been a source of friendships as well as good advice and collaboration.

Also I thank my colleagues in Central South University of Forestry and Technology (CSUFT, Changsha China), for their support, understanding, and encouragement throughout this thesis work. Meantime, I also acknowledge Université de Montpellier, which gave a chance for a PhD study in France.

The training school has been funded by COST Action FP0904 and 1006, where I have harvested a lot of seeds of knowledge and skill. I would also like to show my gratitude to COST Action FP0904 and 1006.

I am forever indebted to my family, especially my parents, my sister, my wife and my daughter for their love, support, understanding, endless patience and encouragement when it was most required.

The work reported in this thesis would not have been possible without the support of Central South University of Forestry and Technology (China), for which I am grateful. Part of this work was supported by COST Action FP1006 and 1303, as well as GDR 3544 "Sciences du Bois", through the Short Term Scientific Mission (STSM). I wish to express my sincere gratitude to all of these.

Titre: Associations tanins-bore pour des produits de protection du bois à faible impact environnemental

RESUME

Le bois est un matériau renouvelable et très polyvalent dans ses utilisations. En raison de ses origines naturelles, il est biodégradable et doit être protégé contre les agents biotiques et/ou abiotiques afin de prolonger sa durée de service.

Les associations tanin-bore peuvent être considérées comme une formulation innovante pour la protection du bois, constituant ainsi des traitements de préservation respectueux de l'environnement. Ces associations aqueuses de tanins (matériau d'origine naturelle) et de bore (sous forme d'acide borique), augmentent la fixation du bore dans le bois. En outre, l'acide borique est en partie fixé sur le réseau de tanins, auto-condensés dans le bois, et conserve une mobilité suffisante pour maintenir son activité biologique. Ces associations ont été étudiées pour leurs applications en milieu extérieur, au-dessus et dans le sol, mais aussi pour leur capacité de protection au feu.

Une formulation originale de tanin-hexamine et d'acide borique, a montré des effets prononcés vis-à-vis des attaques biologiques et du feu, ainsi que l'amélioration des propriétés mécaniques du matériau. Les comportements au vieillissement naturel et artificiel du bois ainsi traité ont été étudiés, et suivis d'essais de résistance vis-à-vis des termites. Dans cette étude, un vieillissement constitué par une percolation de gouttelettes d'eau (pendant 48h), a été réalisé sur un bois traité, afin de comparer sa résistance biologique à celle du bois traité et vieillit artificiellement et naturellement. Les résultats des tests termites (EN117 et/ou EN 118) ont montré que (1) le bois lessivé par percolation de gouttelettes d'eau contient encore suffisamment de bore pour résister face aux attaques de termites; (2) le bois ayant subi un vieillissement naturel contient assez de bore pour tuer les termites, mais pas suffisamment pour éviter une dégradation (basée sur une évaluation visuelle) et (3) le bois ayant subi un vieillissement artificiel a une teneur en bore située en dessous du seuil d'efficacité du produit et ne perturbe donc pas l'activité des termites.

Une formulation avancée à base de tanin-bore, avec l'ajout d'ε-caprolactame pour rendre le réseau polymère plus souple (et éviter les fissures) a été étudiée pour les mécanismes chimiques mis en jeu, sa résistance biologique au-dessus et dans le sol, et ses propriétés ignifuges. Le polymère de tanin acquiert une structure plus élastique, avec l'ajout ε-caprolactame, ceci ayant été montré par des analyses FT-IR (des analyses RMN 13C ont également été réalisées mais n'ont fourni aucune information satisfaisante), et donne au bois une couleur plus foncée au bois traité. Les traitements tannin-bore modifié avec du ε-caprolactame confèrent au bois, selon les normes européennes en vigueur, une protection à long terme contre la dégradation biologique, même en extérieur. Cette formulation avancée tannin-bore-ε-caprolactame montre également un bon potentiel d'utilisation sur des bois destinés à être mis-en-œuvre en contact avec le sol. Toutefois, l'effet ignifuge de la formulation avancée est réduit par rapport à celle de la formulation d'origine à base de tanin-bore, même si elle reste meilleure que celle du bois témoin. Les modules d'élasticité et de rupture (MOE et MOR) des bois traités avec les différentes formulations à base de tannin-bore-ε-caprolactame n'ont pas été altérés par rapport aux témoins.

Afin d'optimiser les associations bore-tannin pour la protection du bois, la conception de polymères bois-nanocomposite avec des tannins et de la montmorillonite a été tentée. Des analyses de FT-IR et XRD ont été réalisées afin d'identifier les particules de nanoargile présents dans le bois traité par le nanocomposite à base de tannin (WTNC). Par ailleurs, les traces de montmorillonite présentes dans les cellules de bois ont également été étudiées au microscope électronique à balayage (SEM). Par comparaison avec le bois témoin, la résistance en compression des échantillons de WTNC augmente ; la stabilité dimensionnelle est légèrement diminuée ; la mouillabilité est fortement affaiblie ; l'absorption d'eau et l'aptitude au collage dépendent fortement de l'essence de bois utilisée (pin sylvestre vs. hêtre) ; la stabilité dimensionnelle du WTNC est légèrement abaissée et la mouillabilité significativement diminuée. Les résistances fongiques et anti-termites du WTNC sont améliorées à des degrés divers selon que l'on utilise du pin ou du hêtre. La résistance au feu du WTNC est modifiée de manière complexe : la chaleur dégagée (Heat Release Rate) par le bois non traité est plus importante que celle du WTNC à base de pin avant l'apparition du second pic de chaleur dégagée, ensuite, cette dernière devient plus faible que celle du WTNC-pin ; tandis que le taux de chaleur dégagée par le WTNC-hêtre est toujours inférieur à celui du hêtre témoin. Le dégagement total de fumée du WTNC-pin est toujours moins important que celle de son témoin, mais le WTNC-hêtre dégage plus ou moins de fumée par rapport au hêtre témoin, en fonction de la phase de combustion considérée. Les effets de l'ATG ont montré que la température déclenchant le phénomène de thermodégradation du matériau était légèrement augmentée lorsque ce dernier contenait des complexes de résines de tannin et de montmorillonite. Ceci implique que la résistance thermique de ces complexes est améliorée. Les analyses combinant DSC et TGA confirment également ces résultats.

Cette étude a aussi analysé l'impact environnemental de la production des produits de préservation à base de tannin-bore (TB, formulation originale), et considéré une approche du cycle de vie («du berceau à la tombe») de matériaux destinés à l'aménagement paysager traités avec des TB, afin de quantifier les impacts environnementaux. Les résultats obtenus pour les deux méthodes LCIA ont permis une comparaison entre le bois traité par TB et traité par 2 formulations industrielles (ammonium quaternaires ACQ, formulation contenant du chrome Cr), et, le béton. L'utilisation de bois traité-ACQ pour l'aménagement paysager offre un impact environnemental moindre (émissions de CO_2), et le bois traité-TB consomme plus de ressources naturelles. Toutefois, les paramètres influençant le procédé industriel d'extraction de tannins devra être considéré à nouveau, et des essais d'éco-toxicité sur le bois traité TB devront être menés. De plus, une analyse économique sur la viabilité de la production d'un produit de préservation à base de tannin-bore demeure cruciale. Ensuite seulement, il pourra être possible de statuer si le TB est un moyen éco-innovant atténuant le changement climatique en allongeant le stockage du carbone dans le bois traité.

Même si tous ces systèmes d'association tanin-bore développés doivent encore être améliorés du point de vue de leurs compositions chimiques, de leurs performances vis-à-vis des attaques biologiques (insectes coléoptères, essais termites sur terrain, pourritures...), et de leur caractère écotoxique, ils ont montré leur efficacité à augmenter la résistance biologique et la résistance au feu d'un bois.

MOTS-CLEFS: Tannin; Acide borique; ε-Caprolactame; Montmorillonite; Préservation du bois; Propriétés du bois; Analyse du cycle de vie

Laboratoire où a été préparée la thèse:

Laboratoire de préservation des bois,
CIRAD, Unité de Recherches Biomasse, Bois, Energie, Bio-Produits (BioWooEB)
TA B-114/16,
73 rue Jean-François Breton,
34398 Montpellier Cedex 5, France.

Title: Tannins-boron networks for long-term and low-environmental impact wood preservatives

ABSTRACT

Wood is a biological renewable material, very versatile in its uses. Due to its origins, it remains biodegradable and needs to be protected against abiotic and biotic agents for a long service life.

Tannin-boron associations can be considered as an innovative preservative formulation and environmentally-friendly treatment. These waterborne associations of tannins (a natural material) and boron in the form of boric acid increase the permanence of boron in the wood. Furthermore, boric acid is partly fixed to the network of autocondensed tannin in the wood and conserves sufficient mobility to maintain its biological action. These associations have been investigated for their outdoor applications, both above and in-ground, as well as for their ability for fire protection.

An original formulation of tannin-hexamine and boric acid, has proved the pronounced effects against biological attack and fire, as well as improved mechanical properties. The natural and artificial weathering behaviour of such treated wood has been investigated, and followed by biological tests against termites only. In this study, a simulated ageing of water droplets (48h) was performed to compare the biologic resistance of treated wood with the artificial and natural weathering. The termite tests results (EN117 and/or EN 118) showed that (1) the water droplet-aged wood has enough boron to resist termite attacks; (2) the natural weathering wood contain still enough boron to kill the termites, but not even to prevent wood degradation (based on a visual rating) and (3) the artificial weathering wood has a boron content below the biological threshold and termite activity is not disturbed.

An advanced tannin-boron formulation including ε-caprolactam to make the polymer network more flexible (and avoiding cracks) was studied for the chemical mechanisms, biological resistance above and in-ground, fire retardancy. The tannin polymer acquires a more elastic structure after adding ε-caprolactam, which is discussed by FT-IR analyses (^{13}C NMR spectra being inspected but not getting satisfying informations), and give a darker colour to the treated wood. The biological resistance of the tannin-boron treatments modified with ε-caprolactam was shown to give a long lasting protection against wood degradation in outdoor exposures according to relative European norms. The tannin-boron formulation advanced with ε-caprolactam also shows the positive potential in the application of contact ground. However, fire retardant effect of this advanced tannin-boron preservative was negatively influenced with comparison to the original tannin-boron formulation, but still better than control. Modulus of elasticity and rupture (MOR and MOE) of wood treated with tannin/boron/caprolactam preservative were not altered in contrast to control samples.

In order to improve the associations between boron and tannin for wood protection, the conception of wood polymer nanocomposite using tannin, boric acid and montmorillonite tentatively carried out. The analyses of FT-IR and XRD have investigated to identify nanoclay in Wood Tannin Nanocomposite (WTNC). Meanwhile, the trace of montmorillonite in wood cell is also captured by SEM. By comparison with control, compression strengths of WTNC samples increase; water absorption and gluing ability of WTNC depend on the wood species used (Scot Pine vs. Beech); dimensional stability of WTNC is slightly decreased, and

wettability was significantly decreased. Fungal and termite resistance of WTNC are improved to different extents if Scots pine or beech samples are used. Fire retardancy of WTNC is complicatedly altered: Heat release rate of control is higher than treated Scots pine wood before appearing the second peak of heat release, but afterward the heat release rate of control decreases to be lower than treated Scots pine wood; whereas heat release rate of treated beech wood is always lower than control. Total smoke release of treated Scots pine wood is always less than control, but treated beech releases more or less smoke than control, depending on the combustion phase. The effects of TGA proved that the onset temperature of the heat degradation slightly increases in the presence of complexes of tannin resin and organic montmorillonite. This implies that the thermal insulation of WTNC had been enhanced by the complexes. The analyses of simultaneous DSC – TGA also prove these results.

This study also analyses the environmental impacts of producing tannin-boron (TB) preservative (the original formulation) and comparatively introduces the cradle-to-grave life cycle environmental impacts of TB-treated timber as landscaping materials, and uses LCA to quantify such impacts. The results calculated for the two LCIA methods show comparison between TB-treated wood and 2 industrial formulations (quaternary ammonium ACQ, Cr based compound), as well as concrete. The use of ACQ-treated timber for landscape offers lower environmental impacts (CO_2 emission) than others, and TB-treated wood consumes more renewable resources. However, the influential parameters of tannin processing at industrial scale should now be investigated further, and eco-toxicological tests on TB treated wood must be carried out. Additionally, an economic analysis of the development of a commercially-viable tannin-boron preservative is crucial. Only then, a complete statement on whether TB is an eco-innovative way of mitigating climate change by extending carbon storage in treated wood can be ascertained.

Even if all these tannin-boron association systems developed still need to be improved for some point of their chemistry, biological performances (coleoptera insects, field tests with termites, molds…), as well as for their eco-toxicological profile, they have shown to improve the biological and fire resistance of the wood.

KEYWORDS: Tannin; Boric acid; ε-Caprolactam; Montmorillonite; Wood Preservative; Wood properties; LCA

Laboratory which was prepared the thesis:

Laboratory of wood preservation,
CIRAD, Unité de Recherches Biomasse, Bois, Energie, Bio-Produits (BioWooEB)
TA B-114/16,
73 rue Jean-François Breton,
34398 Montpellier Cedex 5, France.

Contents

1. Introduction

Wood is an organic, non-fossil, renewable material of biological origin. Timber is a readily available natural material to a modern industrial and engineering material, with a unique ability to donate to human life both as a material for use and as a crucial component in the natural world of the forest.

Wood is an old material with a great future. Wood has early been one of our most important materials from Paleolithic Period of several million years ago, both for building and for the manufacture of tools, weapons, and furniture (Organ, 1959; Ambrose, 2001; Field and Prostov, 1937). With the development of society, wood is one of the first natural materials people learned to use, and it has never lost its popularity. In the up-to-date world, despite the availability of alternative materials, wood remains a preferential choice when it comes to variety of things and applications. Research and technology are expanding the role for sustainable, renewable wood in non-traditional applications. Wood products are also added to a range of eclectic things, including concrete, plastic, clothing, and metals (Mwaikambo, 2006; Cui et al., 2008; Yeoh et al., 2010; Nyström et al., 2010; Scott et al., 1992). Wood is also being more commonly used for transportation fuels (Mohan et al., 2006; Han et al., 2014).

Wood is better for the environment than steel or concrete in terms of embodied energy, air and water pollution, and greenhouse gas emissions. Responsibly sourced wood helps tackle climate change (Petersen and Solberg, 2005; Gerilla et al., 2007). Wood plays a major role in combating climate change: trees reduce carbon dioxide in the atmosphere, as one cubic metre of wood absorbs one tonne of CO_2; greater use of wood products will stimulate the expansion of global forests and reduce greenhouse gas emissions by substituting for fossil fuel intensive products. Furthermore, in the building sector the production and processing of wood uses much less energy than most other materials, also giving wood products a significantly lower carbon footprint. In fact, wood can be used to substitute for materials that require larger amounts of fossil fuels to be produced. In addition, wood products store the carbon that the growing trees have removed from the air (Kurz et al., 2008; Stockmann et al., 2014).

Wood, owning biological, aesthetic, mechanical, thermal, acoustic, electrical, machining, properties etc., is the most plentiful of the renewable resource for industrial materials. Timber is also durable, versatile and can be cost-effective. From the earliest times, the use of wood has been involved in consideration of quality, cost and availability, as well as the intended use of the product. Scarcity of valuable timber has led to careful and economic use.

As is well-known, wood is the major component of the stems of perennial higher plants. It is a plant tissue, xylem, made up of a vast number of cells produced in the plant growth process by the cambium. Wood and other plant tissues in a matrix primarily contain cellulose, hemicellulose, and lignin, which would be attacked by some decomposed agents can develop the ability to damage natural polymers (Nicholas, 1982; Singh and Butcher, 1991). Wood has a certain durability. But it can be deteriorated by wood destroying organisms, and also by the abiotic factors, such as fire.

To prevent degradation, non-durable wood products used in applications are treated with biocides, where they are yielding to biodeterioration. Providing a wooden object is properly preserved, it will easily outlast its service life.

Wood preservation constitutes an important factor in extending wooden products service-life. It is important that wood protection can progressively benefit the environment by extending the CO_2 storage into the wood. Wood preservatives are important to extend the lifespan of wood products by protecting them from damage by insects, fungi, marine borers, weather and fire. By increasing the service life of wooden products, the storage of Carbone into the wood is extended, contributing to both tackling climate change and forest conservation.

Most of wood preservatives on account of the application of chemicals inherently alter the wood and the environment in some manner (Hingston et al., 2001; Lyytikäinen et al., 2001).

Due to a balanced way, the economic, social and environmental dimensions of sustainable development, this study launched a preservative to seek a set of protective goals to address; plant-based tannin and antiseptic boric acid are to be coherent with and impregnated into the timber. The investigations of tannin-boron preservative provide a great opportunity to properly explore the application in wood preservation industry, especially the low-environmental impact wood preservatives contributions. The thesis aims to illustrate the new wood preservative in seizing this opportunity by compiling, making and analysing available existing information on the wood protection.

Some years ago, the preliminary trials of the tannin-boron preservative started in an integrated research team formed from French Agricultural Research Centre for International Development in Montpellier/France, University of Lorraine in Épinal/France and Salzburg University of Applied Sciences in Kuchl/Austria. In the frame of running programme, several tannin based formulations have been developed to apply as wood preservative through vacuum-pressure impregnation. These original formulations have shown very good preservation properties against biologic attacks and fire and it have also shown improved mechanical properties (Thevenon et al., 2009; 2010; 2011; Tondi et al, 2012a; 2012b).

However, there are still some drawbacks for the use of tannins and boron compounds in wood preservation in order to make them interesting and applicable for industrial use, like their high solubility in water and consequently the high leachability. It is necessary to find the approach of a more performing, environmentally-friendly tannin-born formulation and the advanced development of new bio-friendly, low impact and natural wood preservatives derived from low cost poly-phenolic compounds.

Moreover, the introduction of additives such as montmorillonite in the formulation of the wood preservatives will be analyzed to bring new functionality to the wood material (e.g. fire-resistance, dimensional stability, mechanical strength) without modifying the properties as wood-preservative.

A successful finish of the proposed research project enables knowledge on the usability of various environmentally-friendly tannin based formulations as wood preservatives and the influence of these formulations to the process of timber treatment and final wood properties. Progressively, a cradle-to-grave life cycle assessment is done to identify the environmental impacts of tannin-based preservative-treated timber, to understand the processes that contribute to the total impacts, and to determine how the impacts compare to the primary alternative product. The gained knowledge is essential for further projects to get commercially useable results.

The aim of this work is to study different potential associations to fix boron in the form of boric acid into wood, in order to insure its bio-protection as well as its fire protection. Moreover,

some other properties (physical, mechanical) given to the wood will be checked to ascertain that the treatment is not detrimental to basic wood properties.

The successive 2nd chapter of the thesis will set out a literature review on wood boron-based preservative and its developments. Here, the development of boron pesticide in wood industry, the value-add technology of wood modification applied nano-based clay and the life cycle assessment in wood protection are elaborated by abstracting a large number of previous researches. These evidences are necessary to perform this study, synchronously, they can ensure to have a theoretical basement of these determinations.

Chapters 3 will describe a continuous task to what is explored about tannin-boron preservative about biological properties of weathered timber treated with tannin-boric acid-hexamine associations.

Chapter 4 will present an advanced tannin-boron preservative with ε-caprolactam. The chemical mechanisms involved, the effect against the biological attacks in laboratory and field tests conditions, as well as the fire properties will be explored.

Chapter 5 will describes the nanotechnical value-add wood where tannin-nanoclay resins has been permeated and introduced by a process of vacuum or pressure. The wood blocks added with nano-based organ-montmorillonite are checked by microscopy, and several chemistry analyses. Physical, mechanical, biological properties and fire retardant abilities of this formulation have also been performed.

Finally, Chapter 6 will detail the environmental impact of tannin-boron based formulation through a life cycle assessment.

The concluding chapter synthesizes the results and presents recommendations about how the relatively environmental-friendly preservative might be improved.

2. Literature review

2.1 Introduction

Wood is a material with many advantages but due to its natural origin, it can be degraded by organisms or fire. Wood is one of the most versatile materials available, but wood decay, insect degradation and fire reaction can restrict the use of wood. Thus, in many cases, wood needs to be protected against degradation.

This literature review will go through the nature wood and its chemistry, factors affecting able to deteriorate the wood, and the possibility to treat wood for biological and fire protection with boron compounds in particular.

2.2 Wood as habitat and trophic compartment

2.2.1 Wood constituents

Softwood and hardwood trees are lignified plants and most of their trunk and branches are made of wood. Wood can be described as a group of resistant secondary tissues (for mechanical support, conduction and storing) forming trunks, branches and roots of lignified plants. Wood comes from the cambial tissue (Figure 2-1), and is located between the cambium and the pith (NF B 50-003).

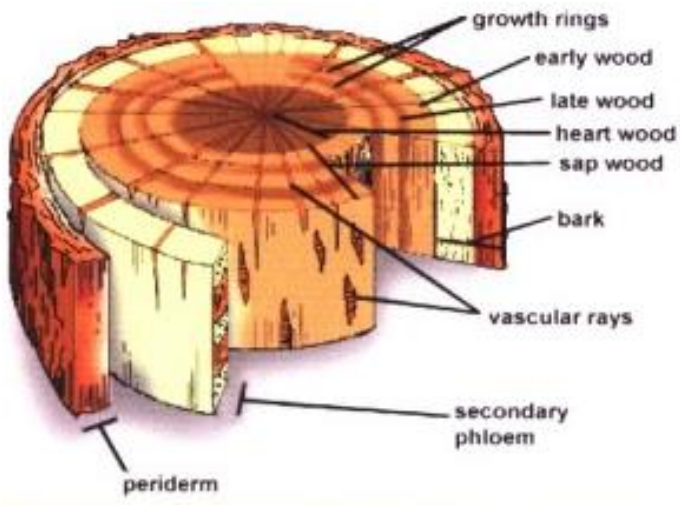


Figure 2-1 Cut-through of a tree trunk (http://www.oakwilt.com)

Wood is essentially composed of cellulose, hemicelluloses, lignin (macromolecular substances) as well as low molecular weight substances represented by the extractives present in the heartwood only (Table 2-1), and the mineral substances.

2.2.2 Cellulose

Cellulose $(C_6H_{10}O_5)_n$ is a linear chain of several hundred to many thousands of β-1,4-glycosidic bonds linked D-glucose units. It is the major constituent of wood (40-45% of its total dry weight)

Due to the non-branched nature and high degree of crystallinity, cellulose is insoluble in most solvents. Water can be bound by hydrogen bonds to the hydroxyl groups on the surfaces of microfibrils but it cannot penetrate the crystalline cellulose (Crawford 1981, Updegraff 1969). However, within the crystalline regions of cellulose, are other regions of less order called amorphous cellulose.

Table 2-1 Chemical constitutes of a few wood species

Constituent		Scots Pine *(Pinus sylvestris)*	Spruce *(Picea glauca)*	Beech *(Fagus sylvatica)*	Eucalyptus *(Eucalyptus camaldulensis)*
Cellulose (%)		40	39.5	47.7	45.0
Hemicellulose	Glucomannan (%)	16.0	17.2	21.4	3.1
	Glucuronoxylan (%)	8.9	10.4		14.1
	Other polysaccharides (%)	3.6	3.0		2.0
Lignin (%)		27.7	27.5	25.5	31.3
Total extractives (%)		3.5	2.1	2.2	2.8

Note: Table 2-1 referred to some publication: Sjostrom 1993, Bodirlau 2008, Vek 2013.

Cellulose has a strong tendency to form intra- and inter-molecular hydrogen bonds by the hydroxyl groups on these linear cellulose chains (Figure 2-2). These non-covalent bonds stiffen the straight chain and promote aggregation. The cellulose molecules get organized in micro-fibrils, which ones also organized in cellulose fibrils.

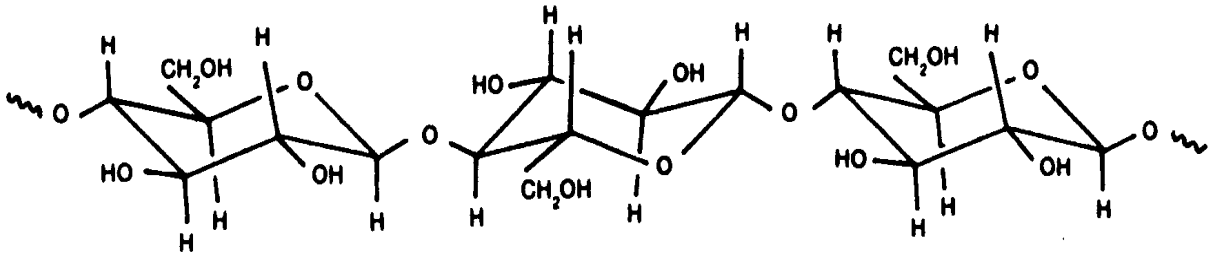


Figure 2-2 Partial structure of cellulose in the 1, 4-β-D-glucopyranose form (Pettersen 1984)

2.2.3 Hemicelluloses

The water-insoluble cellulose microfibrils are associated with mixtures of soluble non-cellulosic polysaccharides, the hemicelluloses, which account for about 25% of the dry weight of wood. In contrast to cellulose, hemicelluloses are made of several sugars in addition to glucose: xylose, mannose, galactose, rhamnose, and arabinose. Hemicelluloses are different from cellulose in their molecular weight and conformation (Figure 2-3).

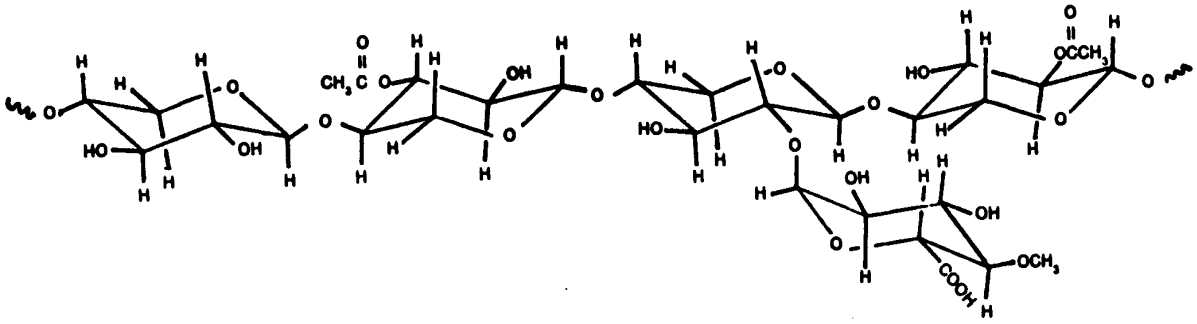


Figure 2-3 Partial structure of a common hardwood hemicellulose, O-acetyl-4-O-methylglucuronoxylan (Pettersen 1984)

2.2.4 Lignin

The third major component of wood, lignin is a phenolic substance consisting of an irregular array of variously bonded hydroxy- and methoxy-substituted phenylpropane units.
Figure 2-4 illustrates the variety of structural components in the structure of softwood lignin. All sugar components can take part in the formation of lignin carbohydrate complexes by covalent linkages between lignin and carbohydrates in wood (Eriksson et al. 1980; Iversen 1985; Iversen et al. 1987). In fact, lignin is embedded in polysaccharide network to ensure tissues rigidity and cohesiveness. It also provides the hydrophobic surface needed for the transport of water (Sjöström 1993).

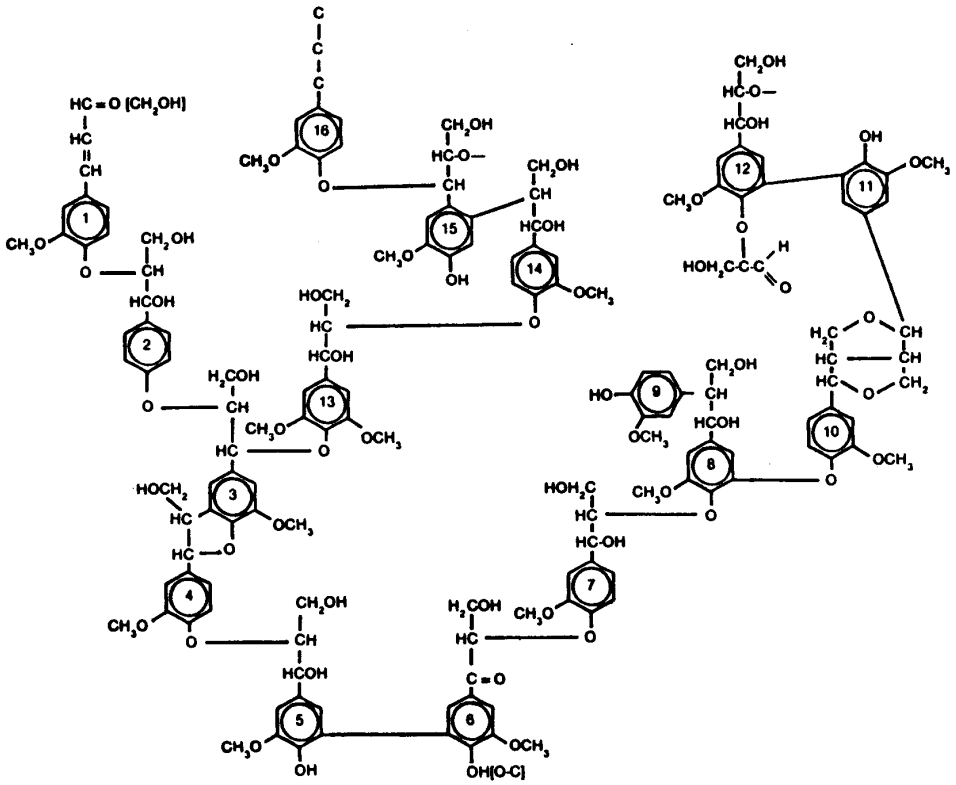


Figure 2-4 Partial structure of softwood lignin (Pettersen 1984)

2.2.5 Low molecular weight substances

2.2.5.1 Extractives

The extractives in wood are one of small-quantity substances other than cellulose, hemicelluloses, and lignin, and are found in the heartwood only. They play an important role in variation of wood properties. They do not contribute to the cell wall structure, and most are soluble in neutral solvents. They may be as much as 20% of the wood of tropical species. They include very different organic compounds: fats, waxes, alkaloids flavonoids, tannins, sugars, and so on (Pettersen 1984). They contribute to wood properties such as color, odor, and decay resistance (Whitney 1968; Hillis 1971).

2.2.5.2 Mineral substances

The mineral substances can be found in the ash after a complete combustion of wood (600-800 ℃). The main minerals found are Si, K P, Ca, Mg, Fe, Al, Ni, Zn…under their oxide, oxalate or chloride form (Pettersen 1984, Sjöström 1993).

Due to its structure and chemical composition, wood can be a habitat and/or a trophic compartment for various organisms.

2.3 Wood deterioration agents

Due to its biological nature, wood remain a biodegradable material, and is often decomposed by a variety of agents, e.g., biotic and abiotic agents acting or in combination under some conditions of exposure and use, especially standing in a wet situation. Some major types of deteriorated agent are responsible for most wood destruction.

2.3.1 Biotic requirements in wood

Biotic agents generally require certain conditions for survival. These requirements include moisture, available oxygen, favorable temperatures, and adequate food (Zabel 1992, Barron 2003, Schwarze and Baum 2000).

Wood moisture content is a major determinant of some types of organisms present and the rate at which they degrade the wood. Generally, wood will not be attacked by the common fungi at moisture contents below20% on average (as water is required for many metabolic processes).

For most of the wood destroying fungi, the temperature must be 20-30 ℃ for optimum growth of most organisms on wood, but some of them can tolerate temperature between 0-45 ℃. In a temperature above 32 ℃, the growth of most organisms declines, although a certain species continue extremely tolerant to prosper up to 40 ℃ (Humphrey and Siggers, 1933). The dry wood insects (coleoptera) do not need high moisture content to degrade the wood, but are affected by the temperature. Their wood destroying larvae will develop at temperatures between 10-30 ℃ on average.

With the exception of anaerobic bacteria, all organisms require oxygen for respiration. Oxygen is essential for the growth of fungi. In the absence of oxygen no fungi will grow. It is well known that storage of wood under water will protect them against attacks by fungi, but marine environment is an exception as a result of marine borers.

Wood is an organic compound and consists of 50% carbon. Most biotic agents that attack wood use it as a food source. Additionally, the presence of nitrogen in wood is necessary for the growth of fungi in wood.

2.3.2 Biotic deterioration of wood

Organisms that attack wood include: bacteria, fungi, insects and marine borers. Bacteria are small single-celled organisms that are among the most common organisms on Earth. It has been shown that they can affect untreated wood exposed in very humid environments, causing increased permeability and softening in the surface of the wood. Bacterial decay is normally an extremely slow process, but it can become serious in situations where the untreated wood is submerged for long periods.

Wood-decay fungi are multicellular microorganisms that spread and propagate via a threadlike mycelium, persisting in soil, wood, and leaf litter. They grow on wood as a microscopic network through holes or directly penetrating the cell wall of wood. The hyphae produce enzymes that degrade cellulose, hemicellulose or lignin, depending on the fungi species, which absorbs the gradient material to finish the process of disintegration.

For most of the wood destroying fungi, once the fungi obtain a sufficient amount of energy from wood, it can form sexual and asexual fruiting bodies that produce spores, allowing the fungi to also disperse by wind or splashing water. Fruiting bodies vary from unicellular spores produced at the end of hyphae to produce perennial fruiting bodies that produce millions of spores. As a result, all wooden structures can be subject to attack in and above ground. Soft rots, inferior fungi, do not produce spores and can only be found in ground.
Amongst all the different fungi (Zabel 1992, Barron 2003), we can find:

- Moulds, surface fungi;
- Staining and discoloration fungi, only present in the sapwood and mainly destroying the starch in the ray parenchyma;
- White rot (fibrous rot) destroying preferentially lignin;
- Brown rots (cubic rots) destroying mainly cellulose and hemicellulose;
- Soft rots most often attacking very wet wood and penetrating into wood rather slowly.

Many insects on earth possess the ability to use wood for shelter (carpenter ants, carpenter bees) or food.
The coleopteran (dry wood insects) will lay their eggs on the surface of wood. The larvae from the eggs will destroy the sapwood only to get the starch from the parenchyma as their source of food. The larvae will grow up to a nymph, which will go out from the wood.
Termites (Isoptera) are different from dry wood insects as the adults degrade the wood. They are a serious problem to the exposure wood. Termites are found nearly worldwide and account for huge economy in damage to wooden structures annually, mostly due to subterranean termites. There are two types of termites: subterranean termites which damage wood that is moist, in direct contact with standing water, soil, other sources of moisture; and dry wood termites which attack and inhabit wood that has been dried to moisture contents as low as 5 to 10% (Berry et al. 1987).
Marine borers, such a as Limnoria or Pholads, can be found in salted waters all over the worlds and can create also important damages (Menzies 1957).

2.3.3 Abiotic deterioration of wood

Wood deterioration is traditionally viewed as a biological process. However, some non-biological factors can also degrade and destroy the timber. The two modes of abiotic degradation include chemical process and mechanical action, even, or two in combination sometimes deteriorate to wood. Like fire invasion, mechanical abrasion or impact, ultraviolet light, metal corrosion by-products, strong acids or bases, etc., these agents can cause substantial damage to wood. (Kirker and Winandy 2014).
The concerned disadvantage of wood is that it easily catches fire. Wood consists of organic compounds which are composed mainly of carbon and hydrogen. They can combine with oxygen and burns. If the temperature of inflammable gas is between 225-260 ℃, it burns with a touch of flame. After the withdrawal of flame it will stop burning. If the temperature increases to 250-270 ℃, it burns with a touch of flame and goes on to burn without a flame. If the temperature increases to 330-520 ℃, wood begins to burn spontaneously. Chemical substances, especially extractives in wood constituents cause the burning point to change. For example, a piece of resinous pinewood can catch fire in lower temperatures. In addition to this, specific gravity and surface mass affect the duration of flame; wood burns harder when the

specific gravity and surface mass and moisture content increase, and vice versa. Besides, a reason for wood combustion is the size of wood element: a face of wood burns and turns into charcoal, which forms on the surface of wood as it burns very effectively insulates heat to transport to another face; therefore large timbers burn very slowly. The outer surface of wood is 1000 ℃ and the interior part is still 40 ℃ when a piece of wood is burning (Tillman 2012). Wood decay, termite attack, ignitability, flame spreading etc. however, can restrict the use of wood. The careful selection and application of an appropriate wood protection system can prevent these concerns for a better service and enable wood-based products to be used in a wide range of applications. Boron compounds preservative systems with high efficiency and low environmental impact are considered a potential in wood protection.
When the natural durability of wood cannot provide a sufficient protection, it is then possible to confer a higher durability to the wood, classically, by using a preservation products applied through a dedicated process. The following review will focus on boron compounds for wood protection.

2.4 Boron in wood protection

2.4.1 Boron

Boron is a chemical element with atomic number 5 and symbol B. Boron element was not isolated until 1808 by Joseph Louis Gay-Lussac (1778-1850) and Louis Jaques Thénard (1777-1857), French chemists, and independently by Humphry Davy (1778-1829), an English chemist; and then this was accomplished through the reaction of boric acid with potassium (Oganov and Solozhenko 2009). Boron is said to be a low abundance element in both the Earth's crust and solar system. This element presented in only 0.003‰ of the earth's crust by mass is not found free in nature, but occurs as orthoboric acid usually in certain volcanic spring waters and as borates in borax and colemanite (Kistler and Helvaci 1994; Corey 2003; Dotsika et al. 2006). Ulexite, another boron mineral, is interesting as it is nature's own version of filament. Important sources of boron are the kernite and borax (Kistler and Helvaci 1994; Dotsika et al. 2006; Sevim et al. 2006). Today, borax is heated to produce boron by carbon, although other methods are used if high-purity boron is required (Wisniak 2005; Ezechi et al. 2011). Nowadays, the largest producers of boron products are in Turkey and the United States (Türker et al. 2013), especially, Turkey has almost 70% of the known boron deposits in the world produces about half of the global yearly demand (Kar et al. 2006; Böcük and Türe 2014).
The boron group is the chemical elements in group 13 of the periodic table. Boron which is one of the simplest of atoms can be made as extremely hard yellow monoclinic crystals, which occurs naturally as 80% ^{11}B and 20% ^{10}B (Hyakutake et al. 1974; Bendel 2005). Elemental boron is rare and poorly studied because the material is extremely difficult to prepare. Chemically Boron is closer to silicon than to aluminum, gallium, indium, and thallium. It has properties which are borderline between metals and non-metals, which is a semiconductor rather than a metallic conductor. Boron is a good conductor at high temperature, but not at ambient temperature (Laubengayer et al. 1943; Widom and Mihalkovič 2008; Häussermann and Mikhaylushkin 2010; Kurakevych et al. 2012).

Boron is present in every part of the environment and it is likely that life evolved in the presence of the element. Boron is probably an especially important element during the evolution of prebiotic structures (Scorei 2012). Boron widely exists in plant and animal tissues and is well known to be essential for the plant growth (Shabala and Munns 2012; Kabu and Akosman 2013). Boron is essential to plant life, but can be herbicidal at high levels. Animals need food or drinking water and absorb boron which occurs naturally in the environment due to the release into air, soil and water through weathering. It was said that boron performed functions in mineral metabolism, in immune response, and in the endocrine system (Nielsen 1997; Hunt 2012; Kabu and Civelek 2012); moreover, boron is not likely to accumulate (Nielsen 1997). When animals absorb large amounts of boron over a relatively long period of time the male reproductive organs will be affected. Studies revealed that the threshold toxicity effect of B in mice and rats (about 4500 ppm as boric acid in the diet for mice) was found to be testicular cell damage and atrophy in males (Mastromatteo and Sullivan 1994). Another analysis of both human and animal data resulted in the suggestion that an acceptable safe range of population mean intakes of B for adults could well be 1 to 13 mg per day (WHO 1996).

2.4.2 Boron applications

Around 200 naturally occurring boron-containing minerals exist on the earth among which the commercially important and frequently used mineral are colemanite, tincal, kernite and ulexite (Kochkodan et al. 2015). These boric ores can be refined into its pure chemical compounds such as boric acid, anhydrous borax, anhydrous boric acid, borax decahydrate and sodium pentahydrate among others. Boron in its combined form of borax has been used since early times. Boron compounds are widely used raw materials in various industries (Simon and Smith 2000; Schubert 2003; Kar et al. 2006).

Early uses were as a mild antiseptic and cleaner because of its detergent and water-softening properties. Later it was used as a soldering flux and ceramic flux because of its ability to dissolve metal oxides. Boron is used in pyrotechnics and flares to produce a green color. Boron has also been used in some rockets as an ignition source. ^{10}Boron, one of the naturally occurring isotopes of boron, is a good absorber of neutrons and is used in the control rods of nuclear reactors, as a radiation shield and as a neutron detector. Boron filaments are used in the aerospace industry because of their high-strength and lightweight. In addition, boron compounds are used for fertilizers, algicides, herbicides and insecticides. Boric powder is used in medicine, leather processing, adhesive, corrosion inhibition, ferrous wire manufacture, fire-proofing and timber preservation. Today boron applications in the world have a lot of means, and it is predominantly risen much more attention as follows (Woods 1994; Wisniak 2005; IBM 2014).

The most important boron compound is sodium borate pentahydrate. Large amounts of this compound are used in the manufacture of fiberglass insulation and sodium perborate bleach. The second most important compound is boric acid, which is used to manufacture textile fiberglass and is used in cellulose insulation as a flame retardant. Sodium borate decahydrate, better known as borax, is the third most important boron compound. These true persalts have

traditionally been blended into powdered detergents in Europe as bleaching agents. In addition, borates have effects on a variety of bacteria, fungi, and insects. Boron has been shown to influence a variety of enzymes, involving both stimulation and inhibition. Borates are used widely in industrial and domestic applications.

2.4.3 Boric preservatives of timber

2.4.3.1 General state

Boron compounds are well known preservative chemicals for timber protection, furthermore, borates available today offer a highly effective and flexible option for both stand alone and more specialized formulations and have received considerable attention in recent years. The principal compound (disodium octaborate tetrahydrate, boric acid, borax) is soluble in water, is odorless and colourless, and diffuses readily into green wood or can be impregnated into dry wood by pressure. Wood treated with borates can be finished (primed and painted). Boron-based wood preservatives are recognized as cheap, easily applicable, biologically active, flame-retardant and, more importantly, environmentally safe preservatives (Lloyd 1993; Laks and Manning 1994).

Actually, the earliest record use of boron in wood protection is possibly a fire retardant, then boron in wood preservation have become more and more important after the Second World War. At present, borate compounds are the most commonly used unfixed waterborne preservatives which can leach from treated wood (Cockcroft and Levy 1973; Drysdale 1994). Boron has some exceptional performance characteristics, including activity against fungi and insects. Treated lumbers with boron-based pesticides are used in areas with high termite, and at higher rates of retention, borates also are used as fire-retardant treatments for wood.

Commercial interest in boron-based wood preservatives firstly arose in Australia and New Zealand where borates were recommended as for an insecticide control (Drysdale 1994). In 1949, the foremost industrial boron-based treatments were performed to use rapidly diffusing boric acid/borax mixtures. Boron treatment was approved for exterior, above ground use in New Zealand in 1958. While boron has many potential applications in framing, it probably is not suitable for many forest service applications because the chemical will leach from the wood under wet conditions. It may be a useful treatment for insect protection in areas continually protected from water, and then this thus limited the development and acceptance of borates treatments to timber commodities (Drysdale 1994). Over the last two decades researchers repeatedly focused on the improvements to the application methods and inclusion of borates in remedial treatments, due to seek for a more operator and environmentally friendly, yet cost effective preservative (Barnes et al. 1989; Drysdale 1994). Researches continuously had the most widespread interests to develop borate formulations that had increased resistance to leaching while maintaining biocidal efficacy (Thevenon et al. 1997, 1998a; Yalinkilic et al. 1999c; Toussaint-Davergne et al. 2000; Robinson et al. 2005; Lake and McIntyre 2006)

2.4.3.2 Boron action against fungi, termite and for fire wood protection

About the biological interaction mechanisms of boron-containing wood preservatives, some compounds of biological significance such as vitamins and coenzymes can react to form complexes with tetrahydroxy-borate ion. In the nature boron is in the form of oxides as either

boric acid or borates (Smith 1985). Boric acid, borax decahydrate, and related borates are moderately soluble in water (Nies and Hulbert 1967), and borates entering the aquatic environment will form undissociated boric acid (H_3BO_3) and the borate anion.

Boric acid is a stable and biologically benign compound, and is mild Lewis acid that it is electron attracting. When bonding with a Lewis base the acid uses its lowest unoccupied molecular orbital, namely boric acid probably ionised as the tetrahydroxy borate anion (Lloyd 1993):

$$B(OH)_3+H_2O \leftrightharpoons B(OH)_4^-+H^+$$

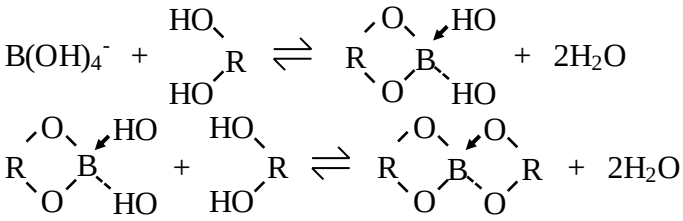
The chemical species present in solution depend on concentration and pH values. At concentrations below 0.025M, mononuclear species $B(OH)_3$ and $B(OH)_4^-$ can only be found; however, at the more than 0.025M, pH values also grow consistent with the formation of polymeric species following (Cotton and Wilkinson 1988; Lloyd 1998):

$$3B(OH)_3 \leftrightharpoons B_3O_3(OH)_4^-+H^+$$

It's also possible that the mixed solutions of boric acid and borates perform a reaction:

$$2B(OH)_3+ B(OH)_4^- \leftrightharpoons B_3O_3(OH)_4^-+H_2O$$

Therefore, in solution boric acid acts as a Lewis acid accepting an OH- to form the tetrahydroxyborate ion $B(OH)_4^-$. Moreover, the toxicity and whereat protection of timber is due to the complexation of $B(OH)_4^-$ with polyols of biological significance in both wood attacking fungi and insects. The polyol compounds of biological significance interacted by the borate anion include vitamins, coenzymes with the oxidized co-enzymes NAD+, NMN+, NADP thought to be the most likely target (Lloyd 1998). The stability of the borate complex formed strongly depends on the type of diol used. According to Lloyd (1993), a strong complex is formed when the diol used involves the hydroxyl groups oriented in such a way that they accurately match the structural parameters required by tetrahedrally coordinated boron. For example, a stable complex is formed by the reaction of boron with compounds possessing cis-diol system. In this case, stable borate complex, cis-diol monoborate ester or bis-diol borate complex is formed:



and

Therefore, boric acid constructs very stable complexes by rapid esterification and this has an effect on extracellular substrates, intracellular substrates, and membranes resulting in altered metabolism, interference with electron transport which eventually synthesis of protein, ATP or DNA/ RNA synthesis in the metabolism of fungi. Chelate complex reactions of borate anion with oxidized co-enzymes probably lead to the biostatic effects of borate through metabolic inhibition.

To termites, boron containing compounds act as a stomach poison. Intestinal protozoa are susceptible, because boron is toxic to the cellulose-digesting organisms and leads to starvation of the host as well as systemic effects. Borates affect termites like a bait-toxicant. Worker termites ingest small amounts of borates and transfer borate tainted food to other colony

members leading to colony elimination. Additionally borates disturb termite's habit of keeping soil foraging tubes moist. Boron readily diffuses into moist soil tubes where many individuals contact boron and are discouraged from building more tubes or feeding (Williams 1997; Freeman et al. 2009). Boron is toxic to termites even at 0.24% mass/mass (m/m) boric acid equivalent (BAE) and causes significant mortality, but termites are not deterred from attacking the timber even at retentions >2.0% m/m BAE, because borates have no repellant action. Higher retentions do not completely eliminate the possibility of minor cosmetic damage (Grace et al. 1992; Grace and Yamamoto 1993; Lloyd 1998; Campora and Grace 2007; Freeman et al. 2009). Borates are also effective against coleopteran wood destroying insects (Lloyd 1998).

So far, no wood destroying organisms have been found tolerant to boron compounds. This is the reason why boron compounds are often used as co-biocides in wood preservation products. Considering fire protection, the mechanism by which inorganic boron compounds function, involves a glassy protective layer formed on the wood substrate to fend off the effects of oxygen and heat (Russell et al. 2007). In fact, several theories about the fire retardant mechanism of boron compounds on wood substrates were proposed decades ago (Browne 1958), it is now commonly accepted that the primary mechanism is the formation of a protective layer on the wood surface at high temperature (Kandola and Horrocks 1996). The mode of action appears to be a combination of the effect of the formation of a glassy inorganic boron film and an increase in char-forming catalytic effect. Boron compounds have a rather low melting point (NPI 2014) and form glassy layers when exposed to high temperatures in fires, which are often intumescent. The char-forming catalytic effect perhaps emerges through the formation of borate esters as well as through the blocking off of volatile fuel release (Cullis and Hirschler 1981; LeVan and Tran 1990). Therefore, the formation of the layer barrier inhibits the flow of combustible volatiles to the fire exposed surface. Additionally, borates and boric acid can also give off water, which provides a heat sink, a fuel

Table 2-2 Some predominant boron efficacy data for fungi

Authors and published year	Descriptions in publication
Kaps et al. 2012	Wood preservative based on rapeseed-oil and boron compounds ensures effective protection against wood rotting fungi (mass loss less than 3%) and discolouring fungi (mould).
Tomak et al. 2011	Combinations of vegetable oils and boron compounds seem to have the potential for engendering a synergetic effect against fungi yielding mass losses of less than 3% against brown rot fungi *Coniophora puteana* for Scots pine and white rot fungi *Coriolus versicolor*.
Chen & Ibach 2010	For non-leached specimens, wood treated with borax/amine/zinc formulations required retention of 1.2% to prevent decay by *Gloeophyllum trabeum* (Gt) and *Trametes versicolor* (Tv), whereas that of DOT/amine/zinc formulations required 0.6% to be effective.
Simsek et al. (2010)	Borate (Sodium tetrafluoroborate (SFB), ammonium tetrafluoroborate, (AFB), and ammonium pentaborate octahydrate (APB)) treated wood showed considerable resistance to the decay fungus compared to that of untreated control specimen.

(Continued)

Table 2-2 *(concluded)*

Authors and published year	Descriptions in publication
Lesar et al. 2009	The results of the fungicidal tests clearly showed that montan wax emulsion and boric acid act synergistically against wood decay fungi.
Lesar & Humar, M 2009	Re-considering minimal boron inhibitory concentrations against wood inhabiting fungi, this study indicated that boric acid had higher efficacy against most of the tested wood decay fungi than reported in previous publications.
Lesar et al. 2008	Boron, quaternary ammonium compounds and ethanolamine based aqueous solutions are effective against blue stain fungi. However, for protection of wood against blue stain fungi, higher concentrations of active ingredients should be used than for protection against wood decay strains.
Lyon et al. 2007	Efficiency against termites is mainly due to boron retention by oil but hydrophobic oil also forms a barrier decreasing fungi penetration. Boron efficacy threshold around 0.7 kg/m^{3}BAE, lower than classical boron treatments thresholds indicates that oil water-repellence reinforces boron biostatic effect.
Temiz et al. (2006)	Decay resistance tests of unleached samples showed that 2%, 1.5% and 1% concentrations of 4-methoxytrityl tetrafluoroborate (MTFB) (15.4 kg/m3, 11.1 kg/m3, and 7.4 kg/m3, retention levels, respectively) gave less than 2% decay of *Postia placenta* and concentrations of 2% and 1.5% less than 2% decay of *Coniophora puteana*.
Kartal et al. 2006	DBF at the highest concentration level (1%) provided limited protection against mold and staining fungi tested (*Aspergillus niger* ASN 5131, *Aureobasidium pullulans* AUP-F24, *Penicillium funiculosum* PEF-9644, *Ceratocystis pilifera* CPI 6702, *Alternaria alternata* ALA 4026, and *Trichoderma viride* TRV 4847), however, it was effective for only short-term protection (1 or 2 weeks) at 0.1% concentrations. DBF was not effective in preventing mold and stain fungi at the lowest concentration tested (0.01%).
Kartal et al. 2005	Both didecyl dimethyl ammonium tetrafluoroborate (DBF) and didecyl dimethyl ammonium chloride (DDAC) at 1%concentration provided protection against the fungi tested (*Aspergillus niger* ASN 5131, *Aureobasidium pullulans* AUP-F24, *Gliocladium virens* GLV 9645, *Penicillium funiculosum* PEF-9644, *Rhizopus javanicus* RHN 32, *Ceratocystis pilifera* CPI 6702, *C. peceae* CEP 8682, *Alternaria alternata* ALA 4026, *Trichoderma viride* TRV 4847, and *Cladosporium herbarum* CLH 4459), however disodium octoborate tetrahydrate (DOT) at all concentrations showed no protection for the entire testing period. With the exceptions of A. niger and A. pullulans, DBF and DDAC were effective for short-term protection (1 or 2 weeks) even at the lowest concentration tested (0.01%) against all fungi tested. For longer protection, higher solution concentrations were needed for these chemicals.

diluent, a propellant for the fuel out of the flame zone, and a blowing agent for the glassy intumescent coating. Borax tends to reduce flame spread but can promote smoldering or glowing, as well as boric acid suppresses smoldering but has little effect on flame spread. Generally, the two compounds are normally used together as a fire retardant.

2.4.3.3 Boron compounds against fungi

In 1920s and 1930s, some American researches firstly investigated boron compounds against blue stain in wood (Cockcroft and Levy 1973; Drysdale 1994). From then until now, a successive study has shown the efficacy of boron compounds against wood-decay fungi. A relatively complete review presented by Drysdale in 1994 had indicated the efficacy of boron-based wood preservatives against fungi. Table 2-2 presents some critical comprehensions of fungicidal test with non-fixed boron in a recent decade.

2.4.3.4 Boron compounds against insect

Efficacy against insects has been demonstrated. Primarily, it was used to control infestations by the powder post beetle (*Lyctus sp.*) in plywood made of tropical hardwoods (Tamblyn and Gordon 1950). It was also applied to control the common furniture beetle (*Anobium sp.*) (Spiller 1948), and later its efficacy developed to prevent termite attacks (Gay et al. 1958; Tamblym et al. 1959). Inorganic boron is listed as a wood preservative in the American Wood-Preservers' Association (AWPA) standards (AWPA 2005), which include formulations prepared from sodium octaborate, sodium tetraborate, sodium pentaborate, and boric acid. The minimum borate (B_2O_3) retention is 4.5 Kg/m^3 for areas with Formosan subterranean termites. Jorge et al. (Jorge et al. 2004) summarise those response threshold of subterranean termite to boron compounds in 2004. Recently, some researchers have carried out boron formulation to termite attacks:

Table 2-3 Some predominant boron efficacy data for termites

Authors and published year	Descriptions in publication
Morris et al. 2014	Samples that were disodium octaborate tetrahydrate (DOT) pressure treated to below the retention required for Formosan termites in AWPA Standards did not perform as well, possibly as a result of poor heartwood penetration as well as below-standard retentions. Addition of permethrin to DOT pressure treatment improved performance.
Gentz & Grace, 2009	The general trend was for the zinc borate (ZB) treatment to have less of an effect on the termites than the disodium octaborate tetrahydrate (DOT) treatment, while were both less harmful than boric acid in these experiments. The boron content of the exposed termites declined by 66–74% after 5 days of feeding on untreated wood, indicating that termites can excrete or metabolize ingested boron over time.
Kartal et al. 2006	Laboratory termite resistance tests showed that 0.5 and 1.0% didecyl dimethyl ammonium tetrafluoroborate (DBF)-treated wood was resistant against the test termites. However DBF treatment at 0.1% concentration was efficient against subterranean termites.
Temiz et al. (2006)	Treatment with 2% 4-methoxytrityl tetrafluoroborate concentration protected against subterranean termites, Coptotermes formosanus Shiraki based on mass losses in both leached and unleached wood specimens in comparison with lower concentration levels.

2.4.3.5 Boron compounds as fire retardant

In wood industry, boron compound was initially considered for flame retardant treatments (Falck and Ketkar 1934), and the commercial fire retardants developing still contain boric acid and borates in various mixtures and concentrations. Boric salts added in wood enhance

the pyrolysis reaction of cellulose through the pathway leading mainly to char formation, thus decrease the heat released and flame spread by the product (Browne 1958; LeVan 1984). Over the last decade, some researched works about boron-containing fire retardants in this field concern with wood: the sole fireproofing efficacy of boron compounds was nearly little considered in treatments of solid wood, but non-solid wood products were modified to protect them in fire by adding some boric salts.

It is well known that a compound of boric acid and borax is a good fire retardant, however, boric acid and borax had more excellent fire retardant effectiveness after natural extractives (brutia pine bark powder, sumach leaf powder, acorn powder, and gall-nut powder) were secondly applied (Baysal et al. 2007). Sodium borate caused improvements in all of the burning criteria according to the ASTM E 160-50 standards and it was determined that sodium borate showed an effective burn retardant characteristic in the Oriental spruce and Uludağ fir. Especially, Oriental spruce in the 10 % solution group had the best percentage result in the loss of weight after burning at 39.88% (Sogutlu et al. 2011). The lowest mass losses for both alder and southern pine specimens treated with a mixture of 5% boric acid and borax aqueous solutions were found to be 68.72% and 72.37%, respectively. It was found that 5% of borax was the most effective treatment in terms of lengthening the time of glowing (Temiz et al. 2008).

Boron compounds mostly act in the condensed phase by redirecting the decomposition process in favor of carbon formation rather than the formation of CO or CO_2 (Camino and Costa 1988; Chen and Wang 2010). However, this formulation cannot prevent oxygen enter into material inner. It's important that a synergetic agent is combined to exert in fireproofing function through melting and coating the surface of material. In wood industry, phosphorus silicon and halogen usually apply with boron as the fire retardant in non-solid wood products: wood plastic composite, fiberboard, particleboard, and so on (Liu et al. 2011; Son et al. 2012; Pan et al. 2014).

2.4.3.6 Practical techniques with boron compounds and boron containing wood preservatives

Today borates have gained worldwide acceptance in vacuum pressure treatments and envelope treatments to construction timber. The main treatment process for preservatives based on boron compounds only (or mainly) is the dip-diffusion process. However, as boron compounds are used as co-biocides in a large range of formulated wood preservatives, the treatment processes used can be divided to three classes: 1) impregnation of wood with preservatives by an enduring vacuum or overpressure, 2) surface treatment by adding the preservative, and 3) addition of preservative to a product during its manufacturing process (panels mainly). In addition, some novel methods outside the above-mentioned classes present, for example, boron gas treatment, vapor boron treatment and liquid boron (Murphy and Turner 1989; Vinden et al. 1991; Nasheri 1999; Baysal and Yalinkilic 2005).

Boron is used with dip-diffusion process to treat wood, especially refractory species.

In general, the greatly different permeability of preservatives present in individual species of softwoods and hardwoods. Some cells allow liquids to pass through them easily and into other cells (Figure 2-5). Types of cells, amount of ray cells, pits and presence of extractives etc. determine preservative chemicals how to permeate. The gymnospermous xylem, to a small

extend, consists mainly of tracheids and parenchyma cells. The latter are generally arranged as uniseriate xylem rays aligned radially in the wood. The ray parenchyma, axially aligned parenchyma cells and resin canals surrounded by epithelial cells sometimes occur in the wood of various genera. Tracheids and fibres are elongated dead cells along tree axis, which provide water conduction, strength and support in the coniferous wood. Different with softwood, the angiospermous wood may possess broad multiseriate xylem rays and/or a characteristic arrangement and concentration of vessels or axial parenchyma (Schwarze and Baum 2000).

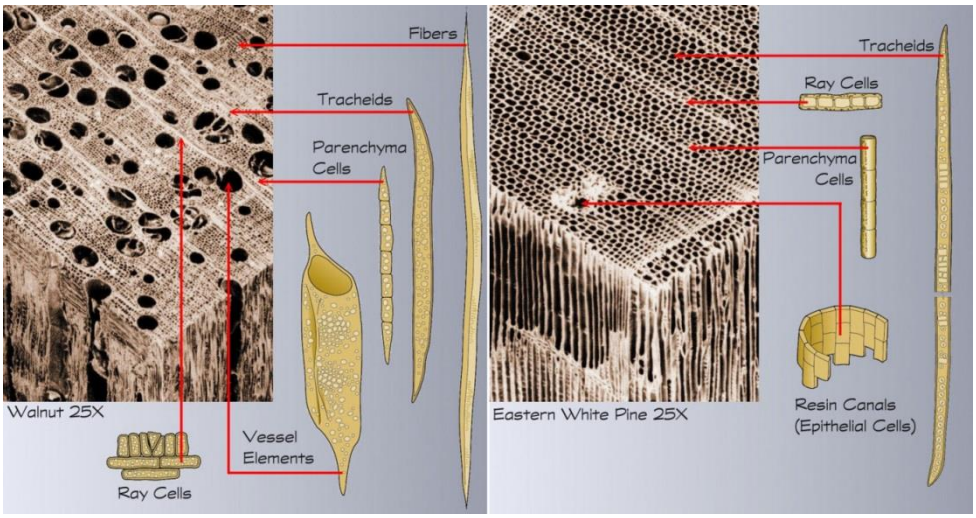


Figure 2-5 The cells that make up hardwood (left) and softwood (right) (Engler 2009)

When impregnating wood with chemicals using a process, the liquid would mainly enter four of the six faces of the cube wood, namely that is, the two transverse faces and the two tangential faces (Figure 2-6). Preservative liquids pass up the length of the tree from cell to cell in the wood through numerous pits in their walls. In most softwood, as these make up virtually all the wood volume, it is possible to fully saturate some softwoods with preservative. In hardwoods, the arrangement of the cells is not as simple as that found in softwoods. Much larger open tubes known as vessels or pores pass liquid from the end to another, additionally and the ray tracheids can also conduct preservatives from a cell to another.

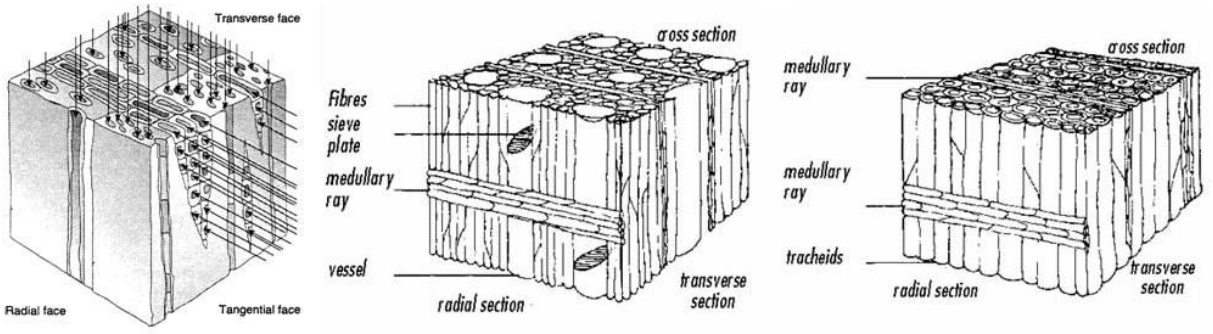


Figure 2-6 Draft of preservative solution flow in wood: liquid entering direction (left), liquid passing cells of hardwood (middle) and softwood (right) (SAWPA 2014, MFS 2015)

Some factors affect wood's permeability by wood microstructure. The cells of the heartwood are inert, often blocked by gums, resins or other chemical compounds and generally contain a high proportion of pits in which the pad on the membrane has moved to one side closing the opening. Therefore, preservative's movement is greatly restricted in hardwood. For most of softwoods, the membrane of pit has at its center a thickened pad large enough to cover either opening to the valve. Under certain circumstances the pad moves over and covers either one

or the other opening, thus restricting the movement of liquids through the valve and therefore movement of liquid from one cell to the next throughout the timber.

Current American standards (AWPA) allow for borates in above-ground environments protected from rain wetting. A wide range of processing options is available for boron treatment. The choice of process depends in the first instance on treatment specification requirements and technical considerations, e.g., the treatability of a particular species by a particular process.

Wood can be protected from the attack of decay fungi, harmful insects, and marine borers by applying chemical preservatives. The degree of protection achieved is influenced not only by the protective value of preservative chemical, but also by the method of application and extent of penetration and retention of the preservative in the treated wood. To obtain long-term effectiveness, the interaction between chemical preservative and wood constitutes is very important, in other words, adequate fixation of chemicals is needed for each wood treatment.

Boron compounds are water soluble, can treat even refractory species, but are easily leachable from treated when in outside, un-protected exposure.

2.4.4 Boron fixation systems for preservative action in wood

The above-mentioned boron-containing preservative systems offer adequate protection to timber in the application of non-ground contact situations. However, it is a great matter of boron leaching of treated wood without any anchored-boron factors. Comprehendingly, it is considered to be only weakly bound to wood components, while boron is introduced in wood with boric acid or borate (Obanda et al. 2008). In fact, loss of effective boron occurs to a serious degree only when timber remains wet environment through its cross-section for long periods while also having an external sink for boron migration. As soon as the boron retention approaches a level too low to drive diffusion, the protective system of wood would be broken. Many studies, therefore, focus on fixing boron to prevent leaching, which may lock the boron resulting in loss of biological efficacy. In 2008, Obanda et al. summarised those strategies which present to resistance to boron leaching but retaining limited mobility of the borate, then they had classified the strategies in Annex A.

In order to improve their susceptibility to leaching, many researchers are still seeking methods to immobilise boron in treated wood applied for outdoor applications. After Obanda getting a review of boron fixation, several investigations have been performed to counteract the problem of boron leachability in wood using several approaches. The system of wood bulking has again been described to reduce boron leachability (Mourant et al. 2009; Mohareb et al. 2011; Liu et al. 2012; Akong et al. 2013; Köse et al. 2013), which is popular with some researchers. Some studies involved the use of boron-silicon compounds to reduce water solubility of boron through formation of insoluble complex (Kartal et al. 2009; Palanti et al. 2012). Other results decreasing boron leachability by a combination (Chen 2008; Lesar et al. 2008; Temiz et al. 2008; Chen and Ibach 2010) present effective, however, the strategy combining non-fungicidal additive indicates that montan wax water emulsion cannot reduce boron leaching significantly (Lesar et al. 2009, 2010). Formation of tannin-boron has also been continued to perform some examinations of boron fixation (Thevenon et al. 2009; Tondi et al. 2012a, b), moreover, some properties of treated wood is enhanced, e.g. compression, fireproofing (Tondi et al. 2012c, 2014).

Along with these developments, restrictions on the use of creosote and heavy-metal based wood preservatives have focused public and government attentions on technological developments in the wood preservation industry, specifically on the availability of more natural alternatives (Directive 98/8/EC 1998; Evans 2003; Schultz et al. 2007; Directive 2011/71/EU 2011). The availability and use of environment-friendly wood preservatives, therefore, is nowadays strictly required.

2.5 Tannin-boron preservative formulation of wood

All aforementioned formulations leave room for the development of a boron fixation system capable of improving the durability of timber treated with it. However, the idea of protecting wood with wood derived natural preservatives has been known since decades (Lotz and Hollaway 1988; Nakayama et al. 2001; Singh and Singh 2012). Especially, a considerable attempt has been carried by the researchers that consider tannins as the ideal solution to protect treated wood with natural substances and boron. In 1988, Laks firstly evaluated a wood preservative of condensed tannin complexed with copper (II) ions (Laks et al. 1988), and then other research groups have sequentially decided to follow a similar investigation line (Scalbert et al. 1998; Yamaguchi and Okuda 1998; Tascioglu et al. 2012). Furthermore, in situ-curing tannin–hexamine formulations were recently tested as wood preservatives for outdoor applications which showed that the high biological activity of these formulations, enriched with a very low amount of boron, is effective in the treatment against high-virulence tropical fungus such as *Pycnoporus sanguineus* (Thevenon et al. 2009) and termites (Tondi et al. 2012b).

While comparison with the retention of boron alone in wood clearly indicate that B forms organic complexes in which it is linked to active sites in wood components by a weak O-bridges (Obanda et al. 2008), the fixation of tannin-boron in wood depends on the tannin polymer, which the reaction of autocondensation of flavonoid tannins induced by weak Lewis acids confirms that boric acid is fixed onto the tannin matrix and has certain mobility of the boron against fungi (Masson et al. 1996). Pizzi and Baecker (1996) present that the complexation of the boric acid with the model compound of the B-ring of tannin is the favourite reaction, followed by the complexation with the model of guaiacyl units of lignin, and last by the model of the carbohydrates from either the tannin or the substrate (Pizzi and Baecker 1996). In another progressive research of fixing-boron mechanism, boron is possibly covalently connected to the flavonoid network in wood but at least one hydroxyl group of boric acid remaining free (Tondi et al. 2012b).

In the very wide studied domain which proposes to protect wood with natural substances, several tannin-based boron-containing formulations have been developed to apply as wood preservative through vacuum or pressure impregnation. The process requires three simply steps: drying of the wood specimens, impregnation with a tannin-boron hexamine solution and hardening of the polymer in situ for exposition at 103 ℃ for 24 h (Thevenon et al. 2009; Tondi et al. 2012b). Those merits of low-cost plant tannin, low-concentration boron and environmentally friendly preservative especially, give a broad prospect in wood industry. The knowledge is essential for further projects to get commercially useable results.

2.5.1 Tannin

Polyphenols play many different roles in plant biology and human life, including UV protective agents, defensive compounds against herbivores and pathogens, contributors to plant colors, contributors to the taste of food and drink, and pharmaceuticals (Calixto et al. 1998; Hassanpour et al. 2011). Except of some higher molecular weight structures tannins are soluble in water (20-35 ℃). Oligomeric compounds with multiple structure units with free phenolic groups can complex with proteins, starch, cellulose and minerals. Traditional use of tannins as agents for converting animal hides to leather is one manifestation of the most obvious activity of the tannins: their ability to interact with and precipitate proteins, including the proteins found in animal skin. In wood industry, Polyflavonoid tannins which can be hardened both by reaction with formaldehyde or by induced autocondensation, have now been used for over 30 years as industrial thermosetting tannin-formaldehyde adhesives for wood products (Pizzi 1983).

According to their chemical structure and properties, tannins are divided into the three principle groups of tannins, the condensed tannins, the hydrolyzable tannins, and the phlorotannins (Pizzi et al. 1981; Ragan and Glombitza 1986; Athanasiadou et al. 2001; ChaichiSemsari et al. 2011; Hassanpour et al. 2011). It is obvious that there is significant chemical heterogeneity among the tannins illustrated by the representative compounds shown in Figure 2-7.

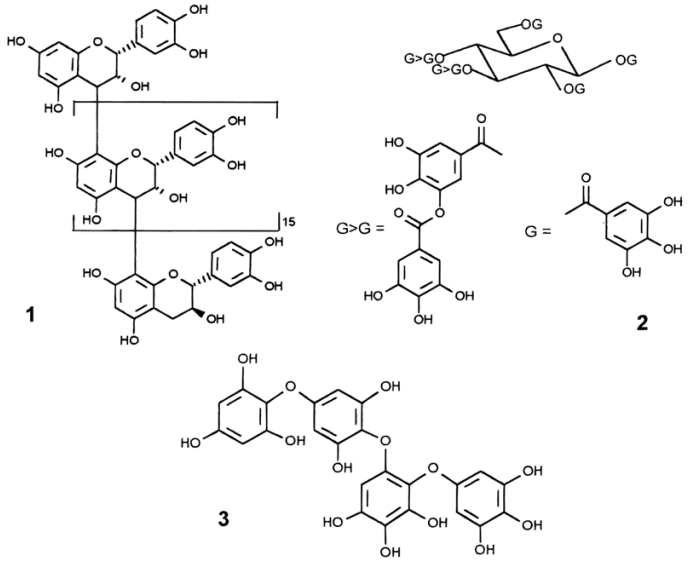


Figure 2-7 Typical tannins. "1" is a typical procyanidin or condensed tannin, made up of catechin and epicatechin. "2" is a hydrolyzable tannin, made up of a glucose core esterified with gallic acid residues. "3" is a phlorotannin, made up of phloroglucinol subunits (Hagerman et al. 1998).

In our study, only condensed tannin will be considered.

Condensed tannins have high reactivity to chemicals such as formaldehyde and constitute more than 90% of the total tannin production in the world (Pizzi 1982).

The condensed tannins are the most common type of tannin found in forage legumes, trees, and shrubs. The main commercial sources for condensed tannins are quebracho (*Schinopsis balansae*) wood and the barks of wattle (*Acacia mearnsii*) and chestnut (*Castanea Sativa*) (Pizzi 1982; Fradinho et al. 2002). Condensed tannins contain complex chemical structures of

polyphenolic compounds comprising groups of polyhydroxyflavan-3-ol oligomers and polymers linked by carbon-carbon bonds between flavonol subunits. The complexity of condensed tannins depends on the flavanoid units which vary among constituents and within sites for interflavan bond formation. While condensed tannin extracts have been used for manufacturing vegetable-tanned leather since the turn of the last century, extension of their industrial use mainly to adhesives, precipitates, depressants and viscosity agents reflects recent development. In wood industry, considering the high molecular, precondensed nature of tannins, the amount of formaldehyde required in their cold- and thermosetting adhesive applications is normally well below that required for the combination of making phenolic resoles from phenol and their setting (Roux et al. 1975).

2.5.2 Development of tannin-boron preservative

The most common commercial condensed tannin is the one found in the mimosa (*Acacia mearnsii*, or *mollissima*) bark extract. Bark extracts by themselves did not cause any reduction in weight loss of pressure-treated wood blocks at the reasonable retentions. However, they do have efficacy as wood preservatives when complexed with boric acid or copper ions (Laks et al. 1988; Pizzi and Baecker 1996). The hydroxy-aromatic chemical composition of tannin has shown similar reactions to the ones found in phenols: hardeners such as formaldehyde, hexamine and glyoxal can crosslink the oligomers to produce macromolecules; furthermore, this chemical property has been the key for the development of tannins in resin formulations (Pichelin et al. 1999). Following the original work of Laks (Laks et al. 1988) other research groups have decided to follow a similar investigation line (Yamaguchi and Okuda 1998; Taylor et al. 2006; Tascioglu et al. 2012).

The main drawback of this idea has always been the high leachability of the tannin. Their extremely high solubility in water (often more than 50 % by weight) rendered these molecules unsuitable as wood preservative (Tondi et al. 2013b). However, the discovery of Pizzi and Pichelin et al. (Pizzi 1980; Pichelin et al. 1999) related to the polymerization of poly-flavonoids has been possible to combat the long-standing leaching problem of tannin and then the interest of this approach in wood protection raised again. The technology that matches to this tannin property consists in infiltrate of the activated oligomers of flavonoid in the wood with a successive in-situ polymerization catalysed by heat (Thevenon et al. 2009).

The fixation of boron compounds is crucial to keep using these active ingredients. If their eco-toxicological profile is well accepted in the USA, Canada, Australia, New-Zealand, it is not the case in Europe. In 2008, boron compounds have been classified as reprotoxic category 3 (Directive). Boric acid can be used at 5.5% w/w only. Then using boron at low level must implies its efficient fixation on a long term.

2.5.2.1 Boron fixation mechanism by tannin-based resin

Boron fixation mechanism by tannin in wood has also been elaborated by Pizzi and Tondi (Pizzi and Baecker 1996, Tondi et al. 2012b). The principle involved is again to build in the wood a tannin-based solid polymer network of low solubility which might or might not be covalently bonded to the wood matrix. Boric acid accepts electrons from the ether oxygen of the flavonoid unit pyran ring with concurrent and consequent facilitation of base induced heterocycle opening. The reactive site so formed (C2) is blocked, by the charge of the boric

acid counterion, from undergoing the intramolecular bond rotations generally associated with intramolecular rearrangements of the unit (Figure 2-8). The effect hence addresses the subsequent condensation of the reactive site formed away from internal rearrangements and towards condensation with a flavonoid unit in another polymer chain. The reaction occurred with all polyflavonoid tannins leads to cross-linking and networking of the material to a hardened state (Pizzi and Baecker 1996).

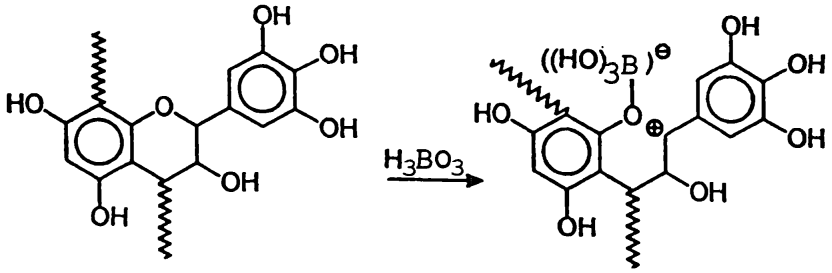


Figure 2-8 Chemical mechanism of polyflavonoid autocondensation induced by boric acid (Pizzi and Baecker 1996)

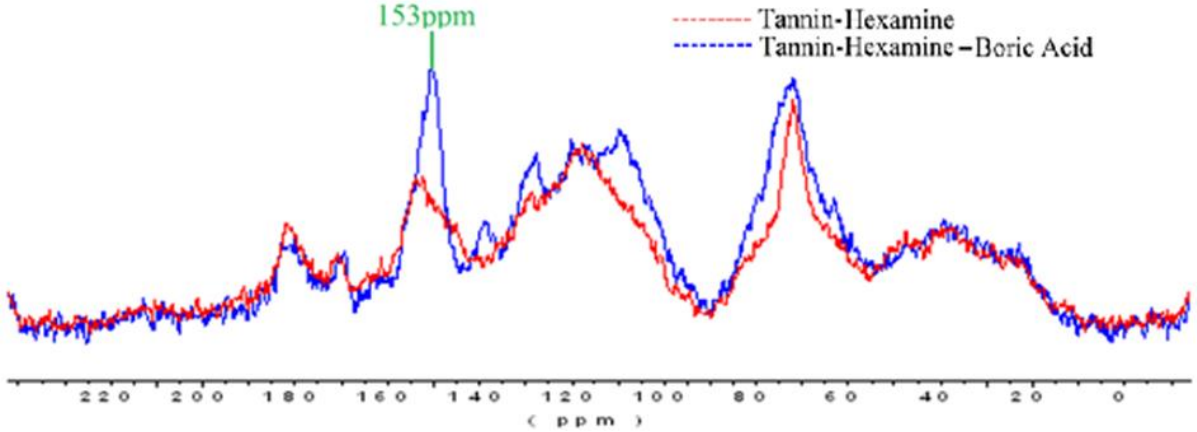


Figure 2-9 ^{13}C-NMR spectra of tannin-hexamine networks with and without boric acid (Tondi et al. 2012b)

In another tannin-based boron fixed formulation, hexamine was introduced to tannin polymerization to induce flavonoid condensation. Tannin-hexamine polymers are condensation products constituted by oligomers of flavonoids interconnected with aliphatic bridges, the latter of which may also include amino groups. The presence of boron catalyses the etherification of the hydroxyl groups of the flavonoid. Figure 2-9 presents that stronger improvement of the signal at 153 ppm is the most important effect of boric acid behaviour in the crosslinking phenomenon. In this reaction the three hydroxyl groups of boric acid can be mono-, di-, or completely substituted. The hypothesis only shows the case in which three hydroxyl groups are etherified (Figure 2-10), but in terms of biological activity it is more probable that at least one of the three branches of boric acid maintains the free –OH group (Tondi et al. 2012b).

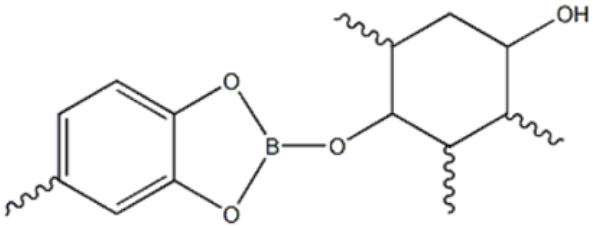


Figure 2-10 Possible adduct between two flavonoids with aromatic and aliphatic parts connected by single or cyclic ether bonds

2.5.2.2 Boron/tannin leaching of treated wood

The restrained leaching of boron due to tannin resin were analysed by some lab-scale methods of leaching (Tondi et al. 2012 a, b). At the beginning of the severe leaching process (5-day guidelines or EN 84), these tannin oligomers will be the first to be leached out. With the leaching proceeding, the loss of rigid tannin polymer also continued but decreased slowly in the final part. All in all, this treatment could leach out up to approximately 35% of the original tannin that was originally retained. Nevertheless, the amount of tannin polymer that remained was still considerable, especially when more concentrated solutions were infiltrated. The greater the content of tannin found in the wood structure, the easier it would be to create a high molecular weight reticule. Observed for both the studied pine and beech, much less material in beech wood was leached out because the polymers can easily crosslink between the vessels, by comparison, the crosslinking of the tannin into the narrow morphology of the tracheids of Scots pine produces thin layers that can leach out with greater ease.

When boron was fixed by tannin network, the leaching of boron occurred much slowly. Like tannin leaching, unreacted boric acid could firstly be leachable, and then partly fixed boron also lost due to rigid tannin polymer broken. However, there was more fixing boron in treated wood with comparison to free-boron treated formulation. Even a milder leaching method applied according to the guideline ENV 1250-2 (1995), the tendency of the curve of free boron showed a greater loss of boron which decreased due to the fact that there was almost no more boron available.

2.5.2.3 Biological properties of wood treated with tannin-boron preservative

The previous studies (Tondi et al. 2012b) indicated that in the case of the test for pine sample treated with only 10% tannin against *C. Puteana* was unsuccessful. The tests have shown that satisfactory results can also be obtained with 0.6% of boric acid but with a stronger polymeric network (20% of tannin in the formulation). In this case the retention level of boron was 3.23 kg/m^3; which was reduced to around 2.52 kg/m^3 after 5-day leaching. It is possible to assert that the value of 2.5 kg/m^3 is the minimal concentration of boron required to reach the standard according to EN113.

There was a report about the results against *Pycnoporus sanguineus* (Thevenon et al. 2009): some formulations which give a small percentage mass loss not only when the treated wood is not leached but also after it has been leached. Thévenon et al. still thought that these formulations based on condensed tannin and hexamine only can be considered as a matrix without the presence of any active ingredient; in addition, formulations based on the complex formed by boric acid with condensed mimosa tannin being networked and hardened by reaction with hexamine. It must also be pointed out that the test was done by using a particularly virulent tropical basidiomycete fungus. This species is considerably more virulent and aggressive than the species (*Coniophora puteana*, *Poria placenta*, *Gloephyllum trabeum*, *Coriolus versicolor*) usually employed for biological tests.

The 20% tannin formulations were effective against insects to different extents. The unleached samples performed according to the EN 47 standard in particular showed an almost complete resistance to the larvae (Tondi et al. 2012a). Nevertheless, the leached sample with ENV 1250-2 in table 2-4 showed interesting results with a larvae survival rate of only 10%. The test with larvae was not satisfactory when the samples were leached according to EN 84.

However, there was a significant resistance to termites in wood treated with the same formulation.

Table 2-4 Biological resistance of 20% tannin-treated samples against insects and termites (Tondi et al. 2012a)

Formulation	Coleoptera (*Hylotrupes bajulus*) Survival rate (%)	Termites (*Reticulitermes santonensis*) Weight loss (%)
Untreated	43	8.1
20% treated (Unleached)	3.3	2.4
20% treated (Leached ENV1250-2)	10	1.5
20% treated (Leached EN84)	30	-

2.5.2.4 The efficacy in preventing weathering degradation of sample treated with tannin-boron preservative

The behaviour during artificial and natural weathering tests is poor: photodegradation process takes place in both polymers of tannin network and lignin in wood; cracks formed as a result of broken tannin polymer can prompt smaller oligomeric fractions to be subsequently leached out. All in all, the tannin-impregnated samples have more stability against discolorations than the untreated ones even if the weathered samples tend to turn grey (Tondi et al. 2012a).

Another study progressively proved the above-mentioned exposition (Tondi et al. 2013a). After a series of contact angle, CIELAB colour system, and ATR FT-MIR and FT-NIR spectroscopy was used to explain the reasons for the poor weathering properties, cross-linked and inelastic tannin networks had been thought to be not suitable photoprotective treatments for wood used outdoors, especially, the weathering had rendered the surfaces more hydrophilic and induced a grey colour.

2.5.2.5 Mechanical and fire properties of wood treated with tannin-boron preservative

Mechanical properties of pine and beech specimens treated with tannin-based formulations have been examined in compression and bending strength tests and surface hardness has also been determined (Tondi et al. 2012c). Scots pine increases its compression resistance by around 30% in compression and by 10% in bending resistance when impregnated with 10% tannin formulations. Beech also increases its mechanical properties: 15 to 20% improvements are reported for samples treated with 20% tannin solutions. The surfaces of the treated wood specimens become harder after each tannin-hexamine impregnation.

A simplified lab-scale fire test was used to evaluate the combustion of wood treated with tannin-boron preservative (Tondi et al. 2012c). The presence of mimosa tannin in wood provided a broad, positive fire-retardant effect: ignition and flame time had significantly been diminished, while the loss of weight under continuous exposure to fire occurred more slowly. The use of boron in the formulation broke down the ember time and slowed down the loss of weight significantly.

In another study, a completely inorganic formulation (disodium octaborate tetrahydrate (DOT)) was compared with new-generation tannin-based wood preservatives in which the flavonoid network was used to fix the boron to wood (Tondi et al. 2014). The ignition process depicted by the dripping tests and by the short exposure test was strongly abated by the glaze

produced by DOT, retardant retention of the tannin-boron formulation but was inferior. Better initial protection was offered by DOT, but as soon as the glaze was burned, the inner wood burned faster than the one treated with tannin-based formulation. The extinguishing properties of DOT were excellent especially at the beginning of the fire when large amounts of DOT were available. The tannin-treated specimens also self-extinguished but with significantly less efficacy. In total, the pine specimens treated with DOT had shown a complete efficacy against fire after all tests were completed. It should also be noted that very positive results have also been achieved by the tannin-based solutions.

2.5.3 Summary of tannin-boron preservative formulation

The original formulations have shown very good preservation properties against biologic attacks and fire and they have also shown improved mechanical properties. Unfortunately the tannin-treated timber is still quite highly affected by artificial and natural weathering exposures. The tannin polymers, being relatively rigid and dark carry to two drawbacks: (i) to mechanically crack the polymer during the continuous dimensional changes occurring when the wood is exposed outdoors and (ii) to higher radical degradation due UV-lights (116, 199). The idea of using ε-caprolactam for rendering the polymers more elastic will be worth considering.

2.6 ε-Caprolactam

ε-Caprolactam (2-oxohexamethylenimine, hexahydro-1H-azepin-2-one) was first described in the 19th century (Dahlhoff et al. 2001). ε-Caprolactam is a synthetic chemical that can be synthesized to fit in a broad range of applications. This important chemical became of real commercial interest in 1938, which was prepared the first spinnable polymer by the polycondensation of caprolactam, thus producing nylon-6 (Dahlhoff et al. 2001). Actually, ε-Caprolactam is the precursor to Nylon 6, which is annually produced 6.7M metric tons in the global nylon market (Mascal 2012). Based on physical and chemical properties, ε-caprolactam can be used in different applications such as textiles, carpets, industrial yarns, fishing lines nets, and so on (BW 2015).

ε-Caprolactam is the popular monomer for the versatile nylon-6 polyamide, which offers excellent properties like a high strength-to-weight ratio, good chemical and thermal stability, and durability. Textile yarn manufactured from nylon-6 exhibits fine drape, resistance to abrasion, high flexibility, chemical and biological stability, and so forth (Dahlhoff et al. 2001). ε-Caprolactam is an irritant and is mildly toxic, with an LD_{50} of 1.1 g/kg (rat, oral). In 1991, it was included on the list of hazardous air pollutants by the U.S. Clean Air Act of 1990. It was subsequently removed from the list in 1993. In water, ε-caprolactam hydrolyzes to aminocaproic acid, which is used medicinally. As of 2011ε-caprolactam had the unusual status of being the only chemical in the International Agency for Research on Cancer's lowest hazard category, Group 4 "probably not carcinogenic to humans" (Goldblatt et al. 1954; GWQS 2002).

ε-Caprolactam is a white crystalline solid and is extremely soluble in water. Recrystallized from ether it yields beautiful transparent rhombs with a melting point of 680 to 700 ℃. The compound tends to take up water in warm, humid air. ε-Caprolactam is readily hydrolysed to

ε-amino caproic acid by heating in dilute mineral acid or alkali. It is stable in aqueous solution at 100 ℃.

ε-Caprolactam possesses the flexible structure (-NH-CO-) formed during in situ reaction of cyclic aliphatic ε-caprolactam with aromatic polymer (Dahlhoff et al. 2001). A ε-caprolactam molecule is a conformationally flexible seven-membered ring, and this usually results in the strong disorder of this ligand in complexes at room temperature (Giniyatullina et al. 2015). The nitrogen and carbon atoms in the seven-membered caprolactam ring were distinguished by the lengths of ordinary C-N and C-C bonds (Tikhomirova et al. 2013). For example, epoxy resin modified with flexible polymers can be cross-linked by ε-caprolactam blocked methylenediphenyl diisocyanate to toughen epoxy system and bismaleimide without an appreciable loss in strength properties (Gupta et al. 2005).

The rigidity of tannin polymer is the key to understanding the process. In the deteriorated condition, the combined effect of wood movement and exasperated agent stresses the polymer and some branches of the polymer network to break, producing lower molecular weight fragments that can be easily leached out. The application of caprolactam as a complicating agent through hydrogen bonding with the hydroxyl groups of the resorcinol, to provide an opportunity for orderly polycondensation (Chow 1983). Thus, the synthesis of a more elastic tannin polymer will be possible for resisting the weathering.

Another way to explore boron compounds fixation, can be the combination with nanoclay.

2.7 Wood nanocomposites generated intercalated structure by montmorillonite

2.7.1 Generalization

In the early 1990s, Toyota Central Research Laboratories in Japan reported work on a Nylon-6 nanocomposite, for which a very small amount of nano filler loading resulted in a pronounced improvement of thermal and mechanical properties (Hussain et al. 2006). Nowadays, nanocomposites offer a new path to improve the traditional counterparts. Because of significantly increased interfacial interaction between inorganic and organic phases and size-dependent phenomena of nanoscale particles, polymer nanocomposites are capable of dramatically improving the mechanical and thermal properties including stiffness and heat resistance, gas and solvent barrier property, flame retardance without losing good ductility of polymer as compared with either homopolymer or traditional microcomposites (Deka and Maji 2011).

Nanocomposites are a new class of composites, which refers at least one dimension of the dispersed particles in the nanometer range (Pavlidou and Papaspyrides 2008). Among all the potential nanocomposite precursors, those based on clay and layered silicates have been most widely investigated, probably because the starting clay materials are easily available and because their intercalation chemistry has been studied for a long time (Theng 1974; Lan et al. 1995; Gorrasi et al. 2002). In fact, four morphology types of composites for layered silicate materials are possible in nanocomposites depending on the strength of the interfacial interaction as follow: aggregated; intercalated; flocculated; and exfoliated (Ray and Okamoto 2003). Montmorillonite (MMT) has the widest acceptability for use in polymers because of

their high surface area and surface reactivity. The polymer matrices can interact with the tetrahedral material, because the negative charge is located on the surface of the silicate layers. In general, low-cost thermoplastic-related monomers such as styrene, acrylate, methacrylate, and methyl methacrylate, can successfully enter into wood cell lumens and form the polymer in situ, but can't penetrate to wood cell or react with wood constituents (Schneider 1994; Couturier et al. 1996). Actually, they are not a true composite due to a simply mixture of two materials. These so-called wood-polymer composites have been enhanced some properties compared to the parent wood. Further information indicated to significantly improve the dimensional stability (Schneider et al. 1991; Deka and Saikia 2000). All in all, these aforesaid technologies possibly give promising practice incorporated nanoclay into wood by having the aid of the presence of monomer.

2.7.2 Structure and characteristics of MMT

Montmorillonite which is one of expandable layered silicates have received considerable attentions in three decades, consisting of very thin layers that are usually bound together with counter-ions. The crystal lattice of 2:1 layered silicates consists of a metal like aluminium or magnesium hydroxide octahedral sheet sandwiched between two silicon oxide tetrahedral sheets, so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets (Figure 2-11) (Beyer 2002; Ray and Okamoto 2003). The layer thickness of each platelet is around 1 nm, and their lateral dimensions may vary from 300 Å to several microns, and even larger, depending on the particulate silicate, the source of the clay and the method of preparation (e.g., nanoclays prepared by milling typically have lateral platelet dimensions of around 0.1–1.0 μm) (Choudalakis and Gotsis 2009). Thus, the aspect ratio of these layers is particularly high, with values greater than 1000 (Alexandre and Dubois 2000, Beyer 2002, McNally et al. 2003, Pavlidou and Papaspyrides 2008).

These layers like the pages of a book form stacks with a gap between them, which called the interlayer or the gallery, where Van der Waals gaps are created. Isomorphic substitution within the layers (Mg^{2+} replaces $A1^{3+}$, or Fe^{2+} replaces Li^{1+}) generates negative charges that are counterbalanced by alkali or alkaline earth cations located in the interlayer (Figure 2-11). In the case of tetrahedral substitution, the negative charge is located on the surface of the silicate layers and, thus, the polymer matrices can interact more readily with tetrahedral than with octahedral substituted material (Choudalakis and Gotsis 2009).

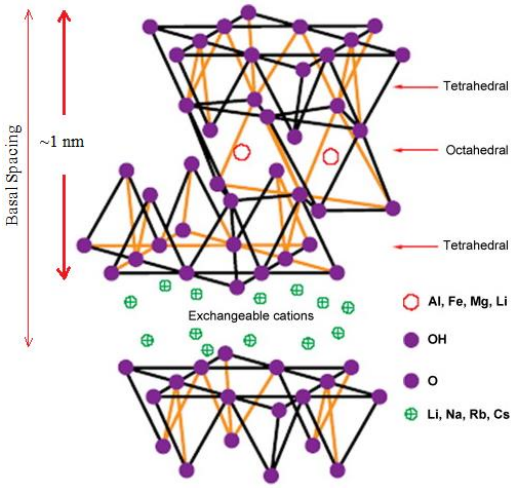


Figure 2-11 The idealized crystal structure of layered montmorillonite (Pavlidou and Papaspyrides 2008)

It is well known that the negative charge of clays is balanced by exchangeable cations, which are usually Na^{+} and Ca^{2+} or K^{+}. To render the layered silicates compatible with non-polar polymers one must convert the hydrophilic silicate surface to organophilic. The replacement of the natural inorganic cations in the clays is achieved by ion exchange reactions with other

organic cations. In order to make the clay mineral compatible with the polymer, at least one of these substituents must be a long carbon chain of 12 carbon atoms or more (Lagaly 1986, Yoon et al. 2007). This organic substituent has two objectives: one is to remove the organic cations from the examined solution systems and the other is to alter the surface properties of swelling clays in order to improve their adsorption capacity. Generally, quaternary ammonium compound is frequently used as an ion exchange with surfactant cations.

2.7.3 Organic modification of MMT

The aforementioned exchanges with bulky alkylammonium ions can solve clays miscible and compatible with other polymers. It can be readily succeeded through ion-exchange reactions that render the clay organophilic. In order to obtain the exchange of the alkylammonium ions with the cations in the galleries, water swelling of the silicate is needed (Kornmann et al. 2001). For this reason alkali cations are preferred in the galleries because 2-valent and higher valent cations prevent swelling by water (Pavlidou and Papaspyrides 2008). Indeed, the hydrate formation of monovalent inter-gallery cations is the driving force for water swelling. Especially mentioned, a purified Na^+ exchange procedure before MMT organ-modifying is observed because much clay may contain divalent cations such as Ca^+ (Zanetti et al. 2000). The non-structural alkali cations can be easily subsituted by other positively charged atoms or molecules.

Usually, the longer the surfactant chain length, and the higher the charge density of the clay, the further apart clay layers will be forced to swell. Surely, the surface modification both increases the basal spacing of clays and serves as a compatibilizers between hydrophilic clay and hydrophobic polymer (Zerda and Lesser 2001). However, the inter-layer distance also depends on the way the alkylammonium-ion chains organize themselves in the organoclay.

2.7.4 Nanocomposite structures and characterizations

Two main types of real nanocomposites based layered silicate and layered silicate can be obtained until now (Beyer 2002; Pavlidou and Papaspyrides 2008) (Figure 2-12). One possesses the intercalated structures which are formed when a single (or sometimes more) extended polymer chain is sandwiched between the silicate layers, which is well ordered multilayer structure of alternating polymeric and inorganic layers. Another gained the exfoliated structures which are obtained, when the silicates are completely and uniformly dispersed in the continuous polymer matrix, for which delamination configuration is of particular interest because it maximizes the polymer-clay interactions, making the entire surface of the layers available for the polymer.

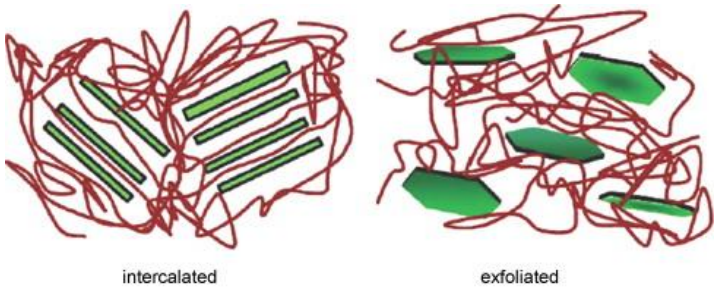


Figure 2-12 Schematic illustrations of two different types of polymer-clay nanocomposites (Pavlidou and Papaspyrides 2008)

In order to characterize the structures of nanocomposites two complementary analytical techniques are used: X-ray diffraction (XRD) and transmission electron microscopy (TEM) (Beyer 2002). XRD is commonly used to identify intercalated structures by determination of the interlayer spacing, and occasionally to study the kinetics of polymer melt intercalation (Ray and Okamoto 2003). TEM observes those representative cross-sections of the sample when XRD difficultly inspect.

In comparison with the gap of the organclay used, the intercalation of the polymer chains increases the interlayer spacing leading to a shift of the diffraction peak towards lower angle values, according to Bragg's law (Beyer 2002; Pavlidou and Papaspyrides 2008). In such intercalated nanocomposites, the repetitive multilayer structure is well preserved, allowing the interlayer spacing to be determined by XRD (Figure 2-13). However, featureless diffraction peaks are visible in the XRD diffractograms of exfoliated structures because the spacing between the layers is too large or the nanocomposite does not present ordering (Vaia and Giannelis 1997; Alexandre and Dubois 2000; Beyer 2002). In these cases, TEM is properly used to characterize the nanocomposites.

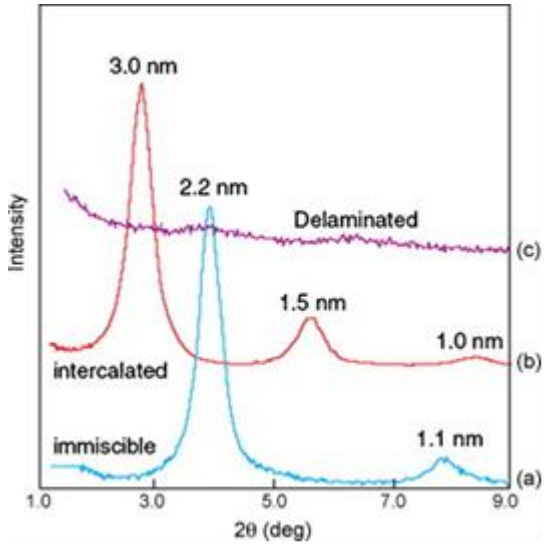


Figure 2-13 Typical XRD patterns from polymer/layered silicates: (a) PE + organoclay → no formation of a nanocomposite, (b) PS + organoclay → intercalated nanocomposite, (c) siloxane + organoclay → delaminated nanocomposite (Beyer 2002; Pavlidou and Papaspyrides 2008)

2.7.5 Wood/clay nanocomposites

In recent years, polymer nanocomposites form an emerging class of mineral-filled plastics containing relatively small amounts of nanometer-sized inorganic particles such as clay. Of course, nanocomposite technology with layered silicate nanoclays significantly attracts a lot of researchers in wood science. Nevertheless, limited data is available on the wood/clay nanocomposites. Wood flour/clay/plastic hybrids by melt compounding, wood fibers with a synergetic combination of clay and coupling agent, solid wood pressed nanoclay and polymer in situ, etc., a few formulations of wood/clay nanocomposite have been investigated (Cai et al. 2007; Kumar and Singh 2007; Lei et al. 2007; Lee and Kim 2009; Kord et al. 2011). The addition of nanoclay to wood-based materials resulted in some improvements of their properties.

The blend nanocomposites were prepared by melt mixing of polypropylene (PP)/wood flour (WF) at 50% weight ratios with various amounts of organomodified montmorillonite (OMMT) (0, 3, and 6 per hundred compounds) in a Hakee internal mixer. Then the samples were made by injection molding. Results indicated that the flexural strength and modulus, tensile strength and modulus increased by addition of 3 per hundred compounds of OMMT, but decreased with 6 per hundred compounds OMMT addition. However, impact strength, water absorption and thickness swelling of the composites decreased with increasing nanoclay loading. X-ray diffraction patterns and transmission electron microscopy revealed that the nanocomposites formed were intercalated. Also, morphological findings showed that samples containing 3 per hundred compounds of OMMT had higher order of intercalation (Kord et al. 2011).

Kumar and Singh (Kumar and Singh 2007) mixed ethylene–propylene (EP), Cloisite 20A©, 5 wt.% maleic anhydride grafted EP (MEP) and 5-15 wt% cellulose fibers, to form an intercalated composite. This investigation indicated that the clay gallery spacing increased by an average of 6Å in EP/MEP/clay composite. The addition of cellulose to EP/MEP/clay composite did not further significantly affect the gallery spacing of the nanoclay. In the mixture of cellulose with the thermoplastic clay nanocomposites, the tensile modulus was improved. The addition of the nanoclay to the cellulose containing composites resulted in a 15% decrease of water absorption by the composites.

Cai et al. (Cai et al. 2007) performed an experimental study of solid wood nanocomposite. Nano-meter fillers were ground with a ball-mill before being mixed with the melamine-urea-formaldehyde (MUF) resin and impregnated into the wood. The water-soluble prepolymer was mixed with the nanoclays at a mixing speed to form impregnation solutions. Significant improvements in physical and mechanical properties, such as density, surface hardness, and modulus of elasticity, were obtained for specimens impregnated with MUF resin and nanoclay-MUF resin mixtures. Ball-mill treatment favors dispersion of the nanofillers into the wood, but also appears to interfere with particle-resin adhesion.

In summary, an up-to-date nanocomposite technology can certainly progress the development of wood industry. Until now, the research that nanoclay is inducted into solid wood is subject to the difficulty because of the form of intercalated structure. Thus, it's very important to probe an optimum process of wood impregnation with polymer and nanoclay. Especially mentioned, the aforesaid studies about polymer nanocomposites and wood/polymer nanocomposites involve those polymers, which come from the petrochemical industry. In fact, environment-friendly condensed tannin induced to polymerize in situ, which possesses the unit of flavonoid, will provide a possibility of wood/flavonoid/nanoclay composite (Figure 2-14), which is furthermore green (Hagerman et al. 1998).

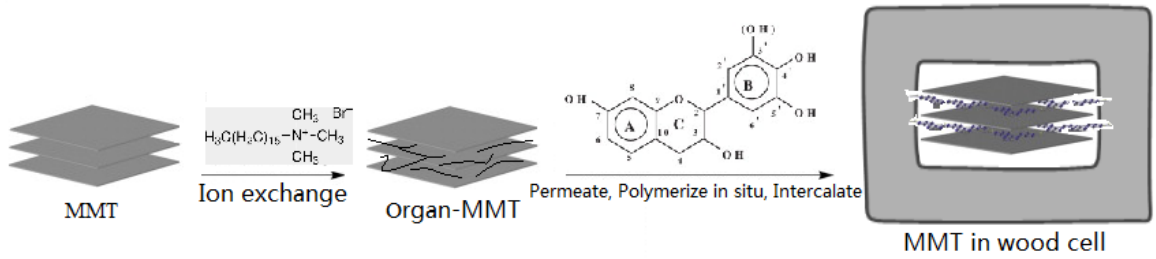


Figure 2-14 Schematic illustrations of wood/flavonoid/nanoclay composite

2.8 Environmental assessment of wood preservation

In this modern world, more and more people have become increasingly concerned about the environmental impacts of our civilized life. Therefore, it is becoming more important to analyze products or services and find ways to reduce humankind's environmental burden. These are just some of the impacts a product has on the environment from cradle to grave during its lifecycle. The five main stages in the lifecycle of a material or product are: raw material acquisition, manufacturing, distribution, use, and end-of-life management. Attributes of a product at different stages of its lifecycle to consider may include: waste and materials, energy, water, other environmental & health impacts, e.g. enhancing indoor environmental quality, reducing environmental impact over the lifecycle, eliminating toxic substances, etc. Among other tools for the assessment of the impacts of mankind's activities on the environment, the instrument of life cycle assessment (LCA) has found considerable interest to the life cycle management of products and services. LCA can perform these analyses and answer important questions about current topics of attraction to the public, such as greenhouse gas emissions. The external use of LCA has become an implement in marketing of products made of different materials (e.g. wood versus plastic or aluminum for windows). We may like it or not, LCA enjoys most attractiveness when a comparison between two products or services is made.

2.8.1 The Concept of Life Cycle Assessment

Given its official term in 1990, when there is an international workshop sponsored by Society of Environmental Toxicology and Chemistry (SETAC), life cycle assessment examines the full spectrum of processes associated with a product from cradle to grave (Fava et al. 1991; Hunt et al. 1996). The International Organization for Standardization (ISO) has been involved in LCA since 1994 (Guinee et al. 2011). Whereas SETAC working groups focused at development and harmonization of methods, ISO adopted the formal task of standardization of methods and procedures. There are currently two international standards (ISO 2006a,b): (1) ISO 14040 (2006 E) - Environmental management - Life cycle assessment - Principles and framework and (2) ISO 14044 (2006 E) - Environmental management - Life cycle assessment - Requirements and guidelines. According to the guidelines of ISO standard, the assessment includes examination of the inflows and outflows associated with a product throughout these

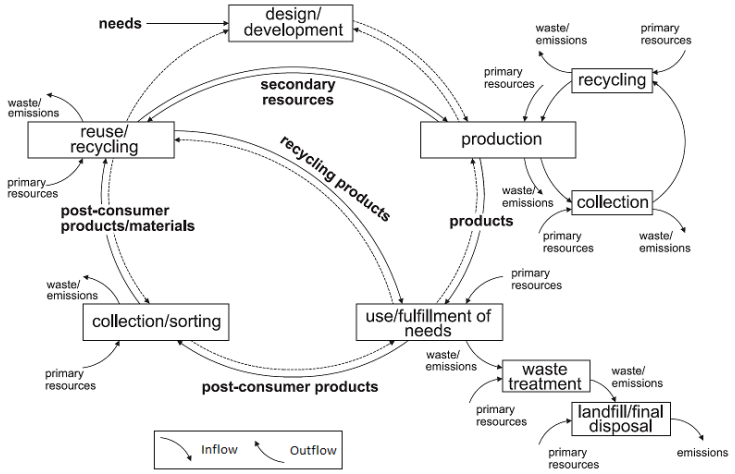


Figure 2-15 Schematic representation of a generic life cycle of a product (Rebitzer et al. 2004)

steps. Figure 2-15 presents a simplified scheme of the product life concept, which is usually referred to as a 'life cycle', as it includes loops between the several life phases. Surrounding such loops, inflows include the resources needed to make and transport the product, while outflows include the emissions and waste the product creates throughout its lifespan.

The ISO 14040 and 14044:2006 originally distinguished four methodological components within LCA: goal and scope definition, inventory analysis, impact assessment, and interpretation, of which interpretation interacts with all other phases in the LCA procedure (Figure 2-16).

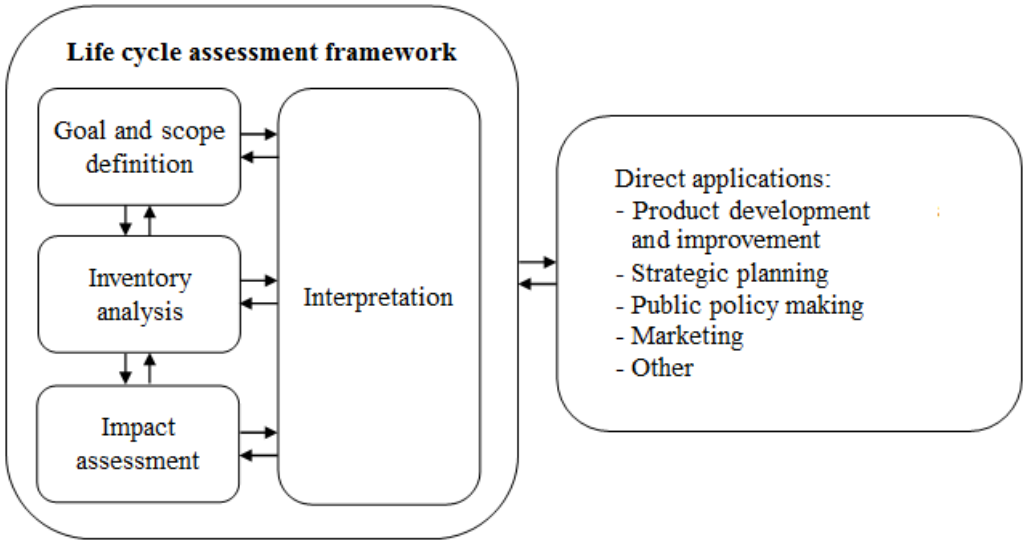


Figure 2-16 Stages of an LCA (ISO 14040)

Firstly, the goal and scope definition of an LCA provides a description of defining purpose, audiences and system boundaries. Secondly, the life cycle inventory (LCI) involves the collection and modeling of data. This phase includes calculating the total amounts of emissions, waste, energy consumed, and resources used throughout the entire flowchart. Thirdly, the life cycle impact assessment (LCIA) evaluates potential environmental impacts and estimates the resources used in the modeled system, which makes the results of an LCA easier to communicate and comprehend. This phase consists of three mandatory elements: selection of impact categories, assignment of LCI results (classifications) and modeling category indicators (characterization) adhering to ISO 14044:2006. Normalization, grouping, weighting and additional LCIA data quality analysis are optional steps. Because impact categories are being compared to one another, and importance is assigned based on factors chosen by the researcher, it is easy to manipulate the process to ignore certain impact categories or favor one product if an accounting LCA is being performed (Pennington et al. 2004). In a life cycle impact assessment (LCIA), there are essentially two methods: problem-oriented methods (mid-points) and damage-oriented methods (end points) (Frischknecht et al. 2007).

Finally, the last stage of ISO 14040 is the interpretation. This stage is necessary to identify the most important aspects of the impact assessment, check the validity of the results, redo aspects of the LCA that need more work, and communicate conclusions and recommendations in appropriate ways. It is important to both compare results to previous studies and improve the quality of the current study.

2.8.2 LCA Tools-Simapro

Simapro is one of the most popular software for LCA. First released in 1990 and developed Dutch consultancy company PRé consultants, SimaPro is the LCA software used by industry, consultancies, and research institutes in English, Spanish, Danish, Greek, French, Italian, German and Dutch. SimaPro can collect, analyze and monitor the environmental performance of products and services by a professional, all-in-one tool for life cycle management. SimaPro can easily model and analyze complex life cycles in a systematic and transparent way, following the ISO 14040 series recommendations (ES 2011).

SimaPro life cycle analysis software can calculate a carbon footprint of many kinds of products and services. Using its customizable parameters and Monte Carlo analytical capabilities, SimaPro can even determine the potential environmental impact that a system or service produces with statistical accuracy. With its ability to determine key performance indicators and issue, SimaPro presents a full view of the potential impact any design will have under realistic conditions. SimaPro comes with several databases, including US LCI, ELCD, Ecoinvent v.2 and LCAfood. Additionally, an IVAM database can be chosen to purchase.

The effect of using cut-off criteria can be analyzed in the process tree or network window in SimaPro. In many LCAs, process trees become large. These process trees contain many processes that have negligible contributions. This can be illustrated by setting the cut-off threshold for displaying processes in the process tree at 0.1 % of the environmental load (for a single score or an impact category). In most cases, only 10 to 30 processes turn out to have a contribution that is above this threshold. Now it becomes much easier to see the relevant issues in the process tree. A similar function can be found in the process of contribution analysis (Goedkoop et al. 2013).

2.8.3 Development of LCA in wood preservation

The use of renewable resources produced on the basis of a sustainable management will be a decisive element for realizing that ideas of sustainable development. Essentially, therefore the main advantage of using renewable resources instead of non-renewable ones, the biological production of the raw materials, should be covered by LCA which claims for analyzing the whole life cycle of a product from cradle to grave. Especially, there is increasing interest in life cycle eco-labelling of many forest products. Efforts for getting back market credibility of wood products, which has been weakened by the discussion about tropical rainforests destruction and adverse environmental impacts of some forest management practices in a lot of countries all over the world, have raised worldwide activities in order to define environmentally appropriate forest management.

It is here assumed that a large proportion of environmental load from forestry lies in the fact that its operations are dependent on techniques that use fossil fuels. Because wood as a biological resource owns a high variability in its inherent material properties, more maintenance and treatments are necessary to guarantee a long-lasting service, especially when exposed outdoors. The technology of wood preservation is an operation in order to prolong the service life of low-durability timber. These treatments may affect the possibilities of a material reuse, which are given and promoted for most of the plastic and metal substitutes

used in the building domain. In LCA's this can lead to some unexpected results when the future recycling potential of alternative materials is rated in an optimistic way (Richter 1995). For instance, the evident benefit of wooden products is their relatively small waste volumes. Most wastes and wood-based materials can be burned after their lifespan. Only the ashes and filter particulates have to be deposited in special landfills. The ashes of used timber products, however, are in most cases contaminated by ancillary materials (paints, preservatives, adhesives, overlays), and should not be used as fertilizer in agriculture (Erlandsson et al. 1992; Kloppenburg and Esser 1994; Hillier et al. 1995).

In recent years the LCA of treated timber is gaining more and more attention, because these process, use and disposal of treated timber involve in environmental issues. In 1992, the first life-cycle comparison of treated timber products was reported (Kuenniger and Richter 1995). Within the past several decades, LCA has been applied widely in examination of the environmental burden of preserved wood product, particularly in comparison with wood plastic composite, steel, concrete, etc. The comprehensive viewpoints about treated timber product are presented as follow.

Kuenniger and Richter (Kuenniger and Richter 1995) pointed out treated roundwood poles had certain environmental benefits and one disadvantage compared to reinforced concrete and tubular steel, while being performed an LCA of utility poles over their entire life. This report thought there was a generally recognized problem in the assessment of life cycle profiles compared to one another, namely, one single environmental effect of treated wood selected for the evaluation cannot lose the priority. The publication emphasized that LCA was a useful approach to quantify these characteristics and should be used for wood products.

In 2011, Bolin and Smith presented a successive comparative LCA for wood treated with preservatives of pentachlorophenol (penta), alkaline copper quaternary (ACQ) and borate (Bolin and Smith 2011a, b, c). In Annex B, a brief comparative description of LCA for those preservative-based timbers is presented below. From table Annex B, compared to preservative-treated timber components of the same size and using the assumptions of these LCAs, with the understanding that assumptions can vary, the selected impact indicators of others all represent different value of environmental impact. Especially, the proportion in used energy of fossil fuel produced borate-treated lumber framing is similar with galvanized steel framing. At end of their disclosure about treated lumber, the suggestion of demolished decking material as fuel is presented in every recommendation, because it is also a style of reducing environmental impact indicators.

Still it is them, namely Bolin and Smith, who expressed two comparative LCAs of wood treated with preservatives of chromated copper arsenate (CCA) and creosote (Bolin and Smith 2013a,b). With comparison to those aforementioned treated timber, the same result was concluded: the use of CCA/creosote -treated wood parts all in all offer priority than similar products under similar assumption. CCA treated wood guardrail posts offer notably lower environmental impacts for fossil fuel use (almost half), net GHG emissions (one-sixth), acidification (approximately half), and ecotoxicity (approximately half) relative to galvanized steel posts. The other indicators are approximately the same; anthropogenic GHG, water use, smog, and eutrophication. However, the use of creosote-treated railroad ties offers lower fossil fuel and water use and lower environmental impacts than similar products manufactured

of concrete and plastic composite, except for the eutrophication impact indicator for plastic composite ties.

In fact, there are other LCAs of wood products relative to wood preservation: timber bridge (Svanæs 2010), floor construction (Petersen and Solberg 2003), wood house (Werner and Richter 2007), and so on. From these reports, more or less impact indicators were anxious to the public. As we have already heard these demonstrations, the wood products industry is facing some tremendous challenges on the environmental front and in the LCA arena.

2.9 Summary of literature review

Responsibly sourced wood is a renewable, versatile, beautiful, cost-effective building material, which helps tackle climate change as result of a significantly lower carbon footprint. However, low-quality wood restricts its outdoor application because of disturbing durability. Therefore, wood treatments with preservatives are required to extend its service life and additionally store the carbon for environment benefits. Nevertheless, environmentally friendly preservatives are still continuously demanded because the public's perception of environment is much more consolidated. The fundamental aim of this review is to elaborate the development of relative to tannin-boron formulation and advanced system proposed in this thesis. It consists in the significant views about tannin-boron preservative application and wood involved timber protection, in particular presented a LCA of preserved wood products. The realization of this review passes through specific objectives: (i) boron efficacy in wood protection, obtained by interpenetrating wood deteriorated agents (ii) tannin anchoring boron through tannin and wood (constituents and structure) interactions; (iii) possible modified formulation of caprolactam additives; (iv) investigations on the nanocomposite based monomer resins (v) studies LCA in wood preservation industry.

3. Termite resistance of aged wood treated with tannin-boron preservatives

3.1 Introduction

Associations between tannin-boric acid, in presence of hexamine, used as wood preservation formulations have shown very good properties against biologic attacks and fire and they have also shown improved mechanical properties (Thevenon et al. 2009, Tondi et al. 2012c). The technology that matches to this tannin property consists in impregnating the activated oligomers of flavonoid in the wood with a successive in-situ polymerization catalysed by heat (Thevenon et al. 2009). One advantage of tannin-boron formulation among several anchor-boron systems is the plant-based tannin flavonoid, as well as the in-situ polymerization without toxic emissions (Pichelin et al. 1999).

The tannin-boron (and hexamine) associations (so called "original formulation") have been well studied, as reported previously.

As a matter of fact, when wood is exposed to outdoor situation, a complex combination of chemical, mechanical and energy factors essentially contributes to what is described as a weathering (Feist, 1983). Photochemical degradation is manifested by an initial color change, followed by loss of gloss, roughening and checking; the depolymerization of lignin and cellulose also lead to reduction in some physical, chemical and biological properties of wood (Müller et al. 2003a, b). Surely, those impregnated wood with tannin-boron preservatives would subjected to weathering under external exposure. Weathering resistance of tannin-boron treated wood has been studied by Tondi et al. (2012a, 2013): (1) the continuous stress due to dimensional movement and to UV-rays shows the sensibility of tannin-boron preservatives to external exposure; and (2) the cross-linked tannin networks are not suitable photoprotective treatments for wood used outdoors.

The work presented in this chapter is included in this wider study of tannin-boron formulations, and is focusing on the evaluation of the remaining efficacy of treatment after long term weathering, as well as laboratory scale weathering.

3.2 Materials and methods

3.2.1 Wood and reagent

Wood specimens of Scots pine sapwood (*Pinus sylvestris*) with different dimensions 150×75×20 mm^3 (L, R, T) for artificial and natural weathering, 50×25×15 mm^3 (L, R, T) for water droplet leaching, were prepared. The samples were placed in a climate chamber (20 ℃ and 65% RH) for constant weight, prior to any treatment.

Unless otherwise stated, chemicals were from Sigma-Aldrich and were of analytical grade. For all assays, deionized water (grade 3, ISO 3696) was used. Mimosa (*Acacia mearnsii*) tannin extract was prepared by Silva Chimica (Italy).

3.2.2 Impregnated solution

The solutions were prepared with 10% and 20% (w/w) of mimosa extract in a solution containing 5% (w/w) of boric acid. The pH of these solutions was always corrected at a pH of 9 using 50% NaOH solution (w/w). Finally, 6% (w/w to tannin) of hexamine was added to the solution under vigorous stirring. The final concentrations of the ingredients are given in table 3-1.

Table 3-1 Proportions of components in the different tannin-boron formulations

Additive / Formulation	Tannin (%)	Boric Acid (%)	Hexamine (%)	NaOH (%)	Water (%)
Free Boric Acid	-	0.49	-	-	99.51
10% Tannin-Boron	10	0.49	0.6	0.49	88.72
20% Tannin-Boron	20	0.49	1.2	0.69	69.34

3.2.3 Vacuum pressure impregnation

At least fifteen water-drop ageing specimens of each series were pressure impregnated. The treatment schedule was (1) 30 minutes of 8 mbar vacuums; (2) pressure slowly increased up to ambient pressure; and (3) 24 hours soaking under ambient conditions. After the impregnation treatment, the excess solution of specimen surface was removed with a blotting paper; and the weights of the treated humid wood blocks were recorded (M_1).

The treated wet samples were kept for at least 24 h 103 ℃ in the oven at to allow the tannin hexamine resin to harden and weighed (M_2).

The retention for each treatment solution was calculated following formula (3-1):

$$R = \frac{(M_1 - M_0) \times C}{V} \quad (3\text{-}1)$$

where R (kg/m^3) is the retention of impregnation wood; M_1 and M_0 (kg) are respectively the initial weight of block and the wet weight of treated sample; C (%) is the concentration of each ingredient in the solution; and V is the volume of the samples (m^3).

The samples for the natural and artificial weathering were impregnated in the same way (Tondi et al. 2012a – BioRessources)

3.2.4 Artificial and natural weathering

Series of three samples of treated and untreated Scots pine samples were exposed to artificial and natural weathering regime.

Artificial weathering was performed in a QUV/spray accelerated weathering tester (Q-Panel Lab Products, Cleveland, OH, USA), equipped with UVA 340 lamps. The selected exposure cycle started with a condensation phase (24 h) to generate moisture stress in the wood substrate, followed by short intervals of UV-light (2.5 h) and water spray (0.5 h) according to EN 927-6 (2006). The duration of the artificial weathering test was 955 h.

These untreated and tannin treated plates were exposed outdoors for 158 days in horizontally inclined weathering racks in Kuchl, Austria. The natural weathering test was performed on a rack inclined at 45 °to the vertical (south exposed).

The weathered specimens were stored in a conditioning room at 20 ℃ and 65% relative humidity (RH) for two weeks prior to termite testing.
This work was performed by Gianluca Tondi in Salzburg University of Applied Sciences (Kuchl, Austria).

3.2.5 Aging test of water droplet

The water droplet test was independently conducted on six samples of each series by a dropper of 40 water droplets per minute and subsequently infiltrated in 48 hours. Figure 3-1 schematically depicted the plan of the test setup. The sample supported by a metal rack was placed below the ring glass. The dropper was positioned about 20 mm above the top surface of the specimen. Four liters of water were delivered during the tests. A stopwatch was used to control the account of water droplet. The leachate was stored a beaker. The leaching waters for 2, 4, 6, 10, 22 and 32 h were collected for the evaluation of the boron loss.

Figure 3-1 Water droplet test setup

3.2.6 Laboratory no-choice termite bioassay methodology

In no-choice feeding tests all specimens were exposed and infested by some subterranean termites of *Reticulitermes flavipes* (*ex. santonensis*). Termites were collected from a French island forest of Ile d'Oléron. Scot Pine samples were used as virulence control. These no-choice test were carried out to evaluate the resistance of wood treated with tannin-boron preservative in a force-feed environment according to the standard EN 117 (2013) and EN 118 (2014).

Figure 3-2 termite essay according to standard EN 117 and EN118 (left: EN 117 termite infestation, middle: weathered sample exposed to termites, right: EN118 termite test on unweathered sample)

EN117 was performed on water droplets leached samples only.
Test containers were prepared with moist sand in the proportions of one volume of water to four volumes of sand. A small piece from the termite breeding box of wood was added to the sand. A ring glass was placed on a vertical wall of the container to avoid direct contact between sand and wood specimen. A group of 250 worker termites and a proportional percentage of soldiers and nymphs (1% to 5%) were distributed carefully in each test container. Afterward, the test containers (Figure 3-2) were placed in the testing chamber at 27 ℃ and 75 % RH.

After 3 days (time for the colony to set up), six replicates per group were exposed to termites in the test containers (1 sample/container)During the exposure time of 8 weeks, weekly observations were carried out to assure appropriate substrate moisture and to monitor the presence of termites and their activity. After the exposure, the samples were removed and the survival rate of the termite worker was calculated. The evaluation of the results was done using a visual rating system (Annex C) according to the guidelines of EN 117 (2013). Additionally, the samples were dried at 103 ℃ and weighed (M_3) to evaluate their mass loss according to Equation (3-2).

$$W_L(\%) = \frac{M_2 - M_3}{M_2} \times 100\% \quad (3\text{-}2)$$

where M_2 and M_3 are the oven-dry weight of the sample before and after the termite attack.
The weathered and non-weathered wood samples were assessed for termite resistance according to the EN 118 (2014). EN118 was the only available option to test biological resistance of weathered samples, as the samples do not need to be cut to perform this test. With this method, only surfaces of samples were exposed to termites. One glass tube (25mm diameter, 110mm length) was glued with colophony on the test specimens (Figure 3-2). Some humid sand (1:4 water and sand, v/v) was added in each tube, taking up at least two-third of the volume of the tube, and 250 termite workers, 1% to 5% soldiers and nymphs were distributed. Test assemblies were kept in a climatic room maintained at 27 ℃ and 75 % RH for eight weeks. There were two or three termite-incubation tubes on each sample. Three controls, namely pine sapwood samples (50×50×10mm^3 (L, T, R)) were used to check the termite virulence. At the end of the test period, the tubes were unsealed and the number of survival was counted in order to determine the survived worker ratio. In addition, each specimen was examined and visually rated using a standard rating system (Annex C) of EN 118 (2014).
These EN117 and EN118 European norms consider bioassays valid where two of three controls reach a termite survival rate exceeding 50%, nevertheless those virulence control specimens correspond to level 4 when visually examined.

3.2.7 Curcumin-salicylic acid reagent for Boron Determination

These samples (at least two samples of each formulation) attacked by termite were conditioned in a room at 20 ℃ and 65% RH. After two weeks, they were split up into two parts.
The reagents needed for testing were created following guidelines published by Smith and Williams (1969).
According to Smith and Williams, 0.28 g of curcumin was dissolved in 100mL of ethanol. This solution was sprayed onto the cut surfaces. A saturated salicylic acid solution was made (salicylic acid in a mixture consisting of 90% ethanol and 10% concentrated hydrochloric acid) and sprayed after the curcumin solution after 30 minutes of drying time. After a 5 minutes time lapse, a colour transition from yellow to fuchsia pink indicates the presence of boron. The curcumin/salicylic acid test has its limitations, namely that it only detects boric acid equivalent concentrations above 0.15 or 0.20% (m/m) (Schoeman, 1998).

3.3 Results

3.3.1 Retention of treated wood

The retentions of $50 \times 25 \times 15$ mm^3 specimens were reported in table 3-2. Significantly highest boron retention was registered for the samples treated with free-boron solution. Furthermore, the retention of boron decreased with the increasing of tannin concentration.

Table 3-2 Retention of treated sample with the tannin-boron preservative

Wood species	Formulation	Total retention(SD) kg/m^3	Boron retention(SD) kg/m^3	Tannin retention(SD) kg/m^3
Pine	0.49% BA	3.70(0.13)	3.70(0.13)	0
Pine	10% Tan. + 0.49% BA	55.64(4.34)	2.48(0.24)	49.24(3.84)
Pine	20% Tan. + 0.49% BA	71.96(4.62)	1.58(0.18)	65.89(3.45)

3.3.2. Termite resistance

Tables 3-3 and 3-4 gave the results from the EN118 and EN117 termite tests.
Both types of test were valid as the controls presented a visual rating of 4, and the survival rate of the termites was above 50%.

Table 3-3 Termite resistance of weathering wood treated tannin-based preservatives after exposure to subterranean termites according to EN118

Treatment (w/w)	Aging method	Survival rate of the termites		Level of attack of the specimen
		Workers (%)	Soldiers(S) and/or nymphs(N)	
10% tannin + boric acid	Artificial weathering	59.2	S. N.	4
20% tannin + boric acid		63.6	S. N.	4
Untreated		56.4	S. N.	4
10% tannin + boric acid	Natural weathering	0	No	4
20% tannin + boric acid		0	No	4
Untreated		62.2	S. N.	4
10% tannin + boric acid	Without aging	0	No	4
20% tannin + boric acid		0	No	4
Untreated		66.2	S. N.	4
Control	No treatment	68.9	S. N.	4

For the ageing by water droplets to wood, significant different results were found for the 3 treatments done.

Only the unleached boric acid treated samples passed the EN117 test (no termite alive, visual rating 1, seen in table 3-4). Nevertheless, as boric acid did not have a repellent action, the termites will have to ingest some treated wood to die. In this case, as boron level was high, the termites will only graze the wood (visual rating 1) before their mortality level reaches 100%. For leached samples treated with boric acid only, even if all termites died, the wood was attacked enough to fail the E117 test.

The tannin-boron treatment solutions contained the same amount of boron (table3-1), but the resistance of the treated samples was driven by the boron retention only (table 3-2). In all cases for tannin-boron formulations (tannin 10% and 20%, unleached and leached samples), the survival of the termites was null, but the surface attack patterns were different. According to rating level and moss loss, 20% tannin treated samples were seriously attacked by termites before and after water-drop ageing.

When boron was subjected to the lab-scale ageing leaching, each formulation did not heavily lose it, even free-boron formulation. Despite poor results considering the visual rating, the mass losses of treated samples were always much lower than the control ones.

Table 3-4 Termite resistance of tannin-treated samples aged by water droplets after exposure to subterranean termites according to EN117

Treatment (w/w)	Aging	Survival rate of the termites		Level of attack of the specimen (%)					Mass loss (%)
		Workers (%)	Soldiers(S) and/or nymphs(N)	0	1	2	3	4	
10% tannin + boric acid	Yes	0	0	0	16.67	83.33	0	0	5.96(1.85)
20% tannin + boric acid		0	0	0	0	0	16.67	83.33	10.18(3.52)
Free boric acid		0	0	0	50.00	50.00	0	0	2.45(0.18)
10% tannin + boric acid	No	0	0	0	50.00	50.00	0	0	4.65(2.15)
20% tannin + boric acid		0	0	0	0	0	50.00	50.00	7.85(4.89)
Free boric acid		0	0	0	100	0	0	0	1.90(0.10)
Control	No	68.92	S. N.	0	0	0	0	100	16.09(0.66)

Considering the EN118 test results, un-weathered and weathered untreated samples behaved like controls for all the criteria of the test. Despite different survival rates, these visual assessments of all treated wood samples (weathered and un-weathered) were rated the level 4, meaning a strong termite attack. After natural weathering, the tannin-boron treated samples still contained enough boron to kill the termites. During performing these tests, termites slowly diminished their activities after three weeks and had no activity for the last five weeks in the tube fixed on each natural-weathered treated sample.

The artificially weathered samples presented a termite survival rate similar to the controls, meaning that there was probably no active boric acid left in the wood.

(Continued)

Figure 3-3 *(concluded)*

Figure 3-3 Samples before and after termite attacks: left images' observations without termite attacks, right images' observations after termite attacks; artificial weathering in b, d and f, natural weathering in h, j and l, unweathering in n, p and r; b, h and n 10% tannin treated wood, d, j and p 20% tannin treated wood, f, l and r untreated wood.

From the figure 3-3, wood specimens were torn off by termites using their mandibles to ingest and store wood in their gut (Varma et al. 1994). Generally, subterranean termites were known to eat along the wood grain (Woodrow et al. 1999), as can be seen in all termite-infested samples after these assays: long strips carved out of wood sample would opt to develop along the grain line of wood; especially in the figure 3-3 (r), these erratic decays in pockets or against the grain evidently proved termites to chew.

With comparison to wood samples before and after termite attacks in the figure 3-3 (a-f), the aggressive tester of spray accelerated weathering seriously broke the network of tannin-boron protection in wood, furthermore, there was no difference of termite infestation between weathered and unweathered area of tannin-treated timbers. All in all, it seemingly looked that termites deteriorated nearly similar to tannin-treated and untreated samples after artificial weathering.

However, natural weathering apparently influenced termite response to tannin-treated and untreated wood from the figure 3-3 (g-l). Nevertheless those nature-weathered samples were infested by termites, this destructive degree was weak than the QUV-weathered and termite-attacked class.

Carefully checking the aspect of the termite degradations on the treated samples, the degraded surface was darker for the naturally weathered samples compared to the artificially weathered samples, indicating the highest presence of tannin (probably still under the form of tannin polymer network.

In addition, someone thought that the unweathered and tannin-treated timber also was chewed by termite, and then tannin-boron formulation could not protect wood. As the aforesaid elaboration, boron was not repellent, so termites must ingest a certain treated wood amount before dying. Levels of activity in the gut generally were regarded as the major site of cellulose digestion in termites. Once the cellulose mixed the boron compounds was involved and continuously accumulated in termite, boron threshold value would arrive, and then termite would not bite wood to starve. Actually, boron is a slow acting preservative to termites and may act not as a feeding repellent (Grace 1997).

3.3.3 Boron inspection by Curcumin-salicylic acid coloration

The coloration results for the water droplets aged samples were presented in figure 3-4.

Figure 3-4 Chromogenic reaction of curcumin-salicylic acid reagent in wood samples: a-10% tannin-treated sample after ageing of water droplets, b-20% tannin-treated sample after ageing of water droplets and c-free boron-treated sample after ageing of water droplets, d-10% tannin-treated sample, e-20% tannin-treated sample and f- free boron-treated sample

Samples treated with boric acid present a strong pink colour, indicating a large amount of boron. In 10% tannin-treated specimen after ageing, latewood was yet fully filled by reddish colour, but this colour indistinctly appeared in 20% tannin-treated block surface. When the

treatment solution contains 20% tannin, the viscosity of the solution was higher and the end-grain penetration of the solution was decreased, leading to a more accentuated shell treatment. For the 10% tannin solution, it seemed that more boron had diffused in the whole section of the samples. However, it was not possible to test if boron was unreacted or not. After the droplets test, the colorations showed that boron was still available in the samples, in accordance with the aforementioned biological tests.

The reagent coloration results for the unweathered and weathered samples are presented in figure 3-5. The penetration trends were the same as explained previously, i.e. 20% tannin solution did not fully penetrate the sample and generated a shell treatment. The coloration of the weathered samples also corroborated the biological tests, the naturally weathered samples still containing a small amount of boron, to the contrary of the artificially weathered samples.

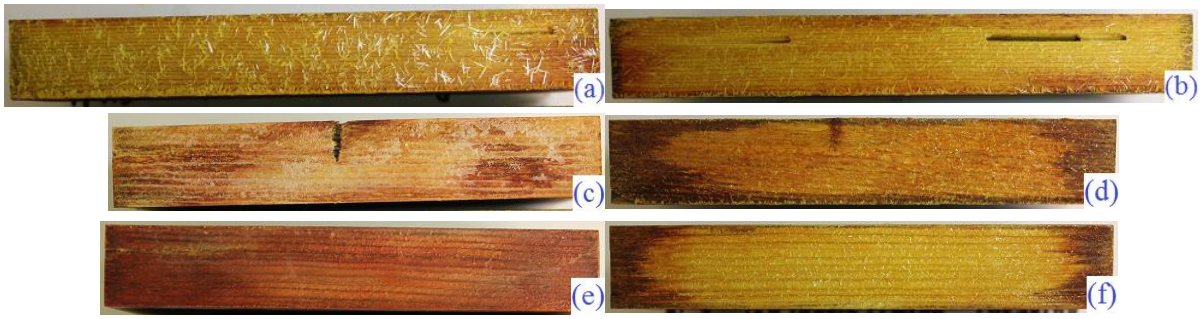


Figure 3-5 Chromogenic reaction of curcumin-salicylic acid reagent in wood samples: a-artificially weathered 10% tannin-treated sample, b- artificially weathered 20% tannin-treated sample, c-naturally weathered 10% tannin-treated sample, d-naturally weathered 20% tannin-treated sample and e-10% tannin-treated sample, f-20% tannin-treated sample.

The curcumin-salicylic acid reagent test showed a deeper color in tannin-treated wood (Figure 3-5 e and f), but it was different that reddish boron reaction to this reagent passed throughout the 10% tannin-treated sample surface, comparatively surrounding the 20% tannin-treated sample. Visual examination under naked eye showed that the curcumin reagent had seeped through to the surface of only treated wood, however, those samples after no matter how ageing react slowly this chromogenic reagent. Figure 3-5 a and b indicate that there was little boron in tannin-treated specimens after artificial weathering excluding the border of sample, moreover, any tannin concentration-treated wood after artificial weathering show same effect to curcumin-salicylic acid reagent. Figure 3-5 c and d distinctly present that much boron existed in tannin-treated wood after natural weathering. Nevertheless subjecting to natural weathering, treated wood can been found some scattered boron, but there was the significant difference between 10% tannin-treated and 20% tannin-treated timber: boron in the middle of 10% tannin-treated sample after natural weathering disappeared, in contrast, the area of 20% treated-treated specimen emerged boron.

3.4 Discussions and perspectives

Understanding the effect of weathering to fixed-boron agent, a progressive aging method was applied in laboratory to measure only water influence. Previous studies about boron leaching in tannin-boron formulation had discussed leaching results of a 5-day method and of ENV 1250-2 (1995). Figure 3-6 showed clearly that the boron was leached out mainly at the beginning of both leaching process because of the incomplete polymerization of tannin resin

(Tondi et al. 2012b). These flavonoid oligomers and the free boric acid will be the first to be leached out. The greater the content of tannin found in the wood structure, the easier it would be to create a high molecular weight reticule, consequently reducing the amount of leached-out boron. Observed for both the studied pine and beech, much less material in beech wood was leached out because the polymers can easily crosslink between the vessels, however, the crosslinking of the tannin into the narrow morphology of the tracheids of Scots pine produces thin layers that can leach out with greater ease.

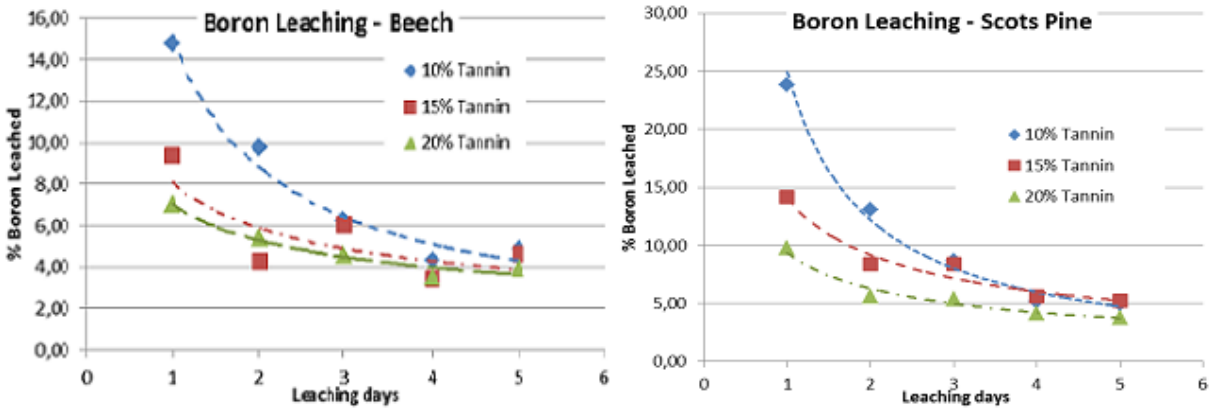


Figure 3-6 Percentage of boron released by tannin-boron treated beech (left) and pine (right) samples monitored every day for the 5 days of leaching (Tondi et al. 2012b)

A milder leaching method was applied according to the guideline ENV 1250-2 (1995). In the figure 3-7, the graphic makes clearly the point that the leaching of boron occurs much slowly when it is fixed with tannin solutions. The tendency of the curve of free boron showed a greater loss of boron which decreased due to the fact that there was almost no more boron available.

When comparing 5-day method and ENV 1250-2 method (Figure 3-8), at the end of the cycle boron leaching by the two methods were really similar: the ENV 1250-2 method is just slightly more vigorous for pine treated samples, while the 5-day leaching affects the beech samples more. Two analysing methods were shown not to be exhaustive for the leaching of the fixed boron, since both methods were able to leach just 30% of the originally penetrated boron.

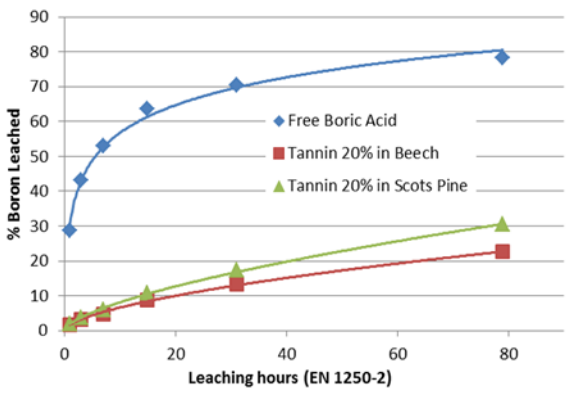


Figure 3-7 Boron leached out during the ENV-1250 leaching test for a 10 g/L boron solution. Free and with 20% tannin for beech and pine (Tondi et al. 2012b)

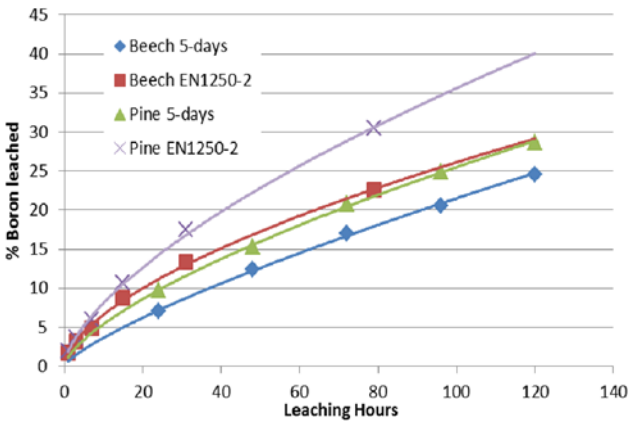


Figure 3-8 Boron leached from beech and pine samples treated with 20% tannin-boron formulations: comparison of leaching efficacy between 5-day method and ENV 1250-2 method (Tondi et al. 2012b)

In the water droplets test, four liters deionized water conducted wood block in 48h continually had leached little boron. This test, based on the guidelines of XP X 41-542 (1995) used to make the percolation of treated materials used as anti-termite barrier, was much milder than ENV 1250-2 and 5-days leaching, as shown by the coloration and termite tests results. Thus, this test cannot be considered as discriminant enough to be used further in our study.
Considering the weathering, the degradation depended on the type of material, but the cause was a combination of factors: moisture, sunlight, heat/cold, chemicals, abrasion by windblown materials, and biological agents, having a synergetic effect (Williams 2005). The weathering process was divided into natural and artificial weathering.
The artificial over natural weathering occurred for several reasons: principally, the tests can run continuously at naturally occurring or higher irradiance than solar radiation, uninterrupted by the natural day/night cycle, seasonal variations, and weather conditions. Temperatures, thermal cycles, humidity, and water exposure also can be manipulated to maximum, but not unrealistic, stress levels. In addition to the ability to manipulate and accelerate weathering conditions on demand, a fundamental benefit of a laboratory test was the reproducibility and repeatability over what was essentially an uncontrolled and variable phenomenon, the actual weather (Ollier 1984, Wypych 2003).
In other words, independent controlled artificial weathering conducted to study the specific response of materials to various weathering factors was more aggressive than natural weathering. In the current study artificial weathering was performed according to EN 927-6 (2006). The energy transferred to the specimens at the predominant wavelength of 340 nm was around 4000 kJ/m2, a value that was equivalent to 150% of Eastern Austria's natural solar radiation in 2002 (Hansmann et al. 2006). However, the aim of this standard was not to simulate natural weathering in a specific region, since the applied water spray was far beyond any practical relevance.
So the high dose of water spray of artificial weathering served mainly for the removal of degraded material from the sample surface but also to produce frequently a cold environment. The high amount of water and continuous ultraviolet easily broke the tannin polymer network in the tannin-treated timber. Although natural weathering can influence the anchored-boron tannin system, it depends on the local climatic conditions.
The protective factors of the tannin-impregnated wood specimens were leached after weathering. It seemed that the key factor was to increase the dimensional stability of the treated tannin-boron samples in order to avoid tannin-boron-hexamine network to break. The effect of weathering conditions stressed the polymer and some branches of the polymer network to break, producing lower molecular weight fragments that can be easily leached out. Thus the rigidity of the tannin polymer was the key to upgrade the tannin-boron formulations in terms of biological efficacy on a long-term run.

3.5 Conclusions

In the investigation of termite resistance, partial boron in weathered wood was not enough to hinder biological deterioration after photoprotective treatments breaks cross-linked and inelastic tannin polymer networks. However, artificial-weathered tannin-treated wood and natural-weathered tannin-treated did not response to termite infesting: remained boron in

tannin-treated timber after natural weathering can kill all termites participated in the testing, but visual rate of sample is arranged 4 class according to EN117; boron in tannin-treated wood blocks after artificial weathering have nearly been leached.

Only water-droplet ageing in 48h cannot totally disturb tannin polymer network.

It was concluded that although tannin-boron formulation had very interesting properties as wood preservatives, tannin-boron formulation was yet not completely suitable for wood used outdoors.

The main reason for the degradation had been proposed. The continuous change in moisture and temperature that occurred during the weathering tests stressed the aromatic polymers of the surface and forced the rigid tannin-hexamine network to break.

Therefore, the rigidity of the polymer was the key to understanding the process, and then more elastic tannin based polymers may be better at protecting wood from photodegradation. An approach can be considered in modifying the structure of the polymer - covalent branches with caprolactam of long chain copolymers.

4. Advanced tannin-boron preservative

4.1 Introduction

Tannin-boron formulation is a promising preservative, which is plant-based and highly-effective. Despite promising biological results in the laboratory, weathered tannin-treated timber was shown to lose its efficacy mainly because of the break of anchored tannin polymer network. Thus the synthesis of a more elastic polymer will be indispensable for the future of this semi-natural wood preservative. ε-Caprolactam can be considered in modifying the structure of the polymer and prolonging the branches of tannin polymer.

ε-Caprolactam is the monomer for nylon-6, most of which is nowadays produced by the conventional cyclohexanone process in large-scale industrial production. The ring opening polymerization of ε-caprolactam with covalent branches could be charged on the branches of tannin polymer to extend it (Pichelin et al. 1997, Tondi et al. 2012). In the present part, advanced tannin-boron preservative will be investigated: chemical mechanism, biological properties and field tests of treated wood.

4.2 Materials and methods

4.2.1 Wood and reagent

Wood samples of Scots pine sapwood (*Pinus sylvestris*) of dimensions 50×25×15 mm^3 (L, T, R) were prepared for the biological and fire tests.

Scots pine sapwood (*Pinus sylvestris*), beech (*Fagus sylvatica*), simarouba heartwood (*Simarouba amara*) and African padauk heartwood (*Pterocarpus soyauxii*) of dimension 100×10×5 mm^3 (L, T, R) were prepared for the field tests only. The samples were placed in a climate chamber (20 ℃ and 65% RH) for constant weight, prior to any treatment.

Unless otherwise stated, chemicals were from Sigma-Aldrich and were of analytical grade (99% purity). For all assays, deionized water (grade 3, ISO 3696) was used. Mimosa (*Acacia mearnsii*) tannin extract was prepared by Silva Chimica (Italy).

4.2.2 Samples of chemical mechanism for tannin-boron polymer modified with ε-caprolactam

Eighteen chemical samples (table 4-1) were prepared according to different reacting formulations of tannin, boric acid (solution 5% w/w), sodium hydroxide (solution 50% w/w), hexamine (solution 33% w/w) and water.

These chemical mixtures were weighed in 50-ml autosampler vials. Chemicals were vigorously stirred to dissolve the solids. All different solutions were placed in an oven at 103 ℃ to allow chemicals to react completely.

The obtained chemicals or polymers were crushed with a mortar, and the powders were divided to be analysed with FT-IR and ^{13}C-NMR.

The chemical specimens were sealed with Teflon-lined caps and kept a chamber at 20 ℃ and 65% RH.

Table 4-1 Information of samples inspecting chemical mechanism of polymer

No °	Solution compositions	Weight ratio	pH
1	Tannin, water, sodium hydroxide	1:1:0.05	nd
2	Hexamine, water, sodium hydroxide	1:1:0.02	nd
3	Caprolactam, water, sodium hydroxide	1:1:0.05	nd
4	Tannin, hexamine, sodium hydroxide, water	1:1:0.1:2	nd
5	Tannin, caprolactam, sodium hydroxide, water	1:1:0.1:2	nd
6	Caprolactam, hexamine, sodium hydroxide, water	1:1:0.1:2	nd
7	Tannin, caprolactam, hexamine, sodium hydroxide, water	8:8:4:0.1:20	nd
8	Tannin, boric acid	2:5	nd
9	Tannin, sodium hydroxide, boric acid	2:0.1:5	nd
10	Tannin, sodium hydroxide, boric acid	2:0.5:5	nd
11	Hexamine, boric acid, sodium hydroxide	1:1:0.02	nd
12	Caprolactam, boric acid, sodium hydroxide	1:1:0.05	nd
13	Tannin, hexamine, boric acid, sodium hydroxide	1:1:2:0.1	nd
14	Tannin, caprolactam, boric acid, sodium hydroxide	1:1:2:0.1	nd
15	Caprolactam, hexamine, boric acid, sodium hydroxide	1:1:2:0.1	nd
16	Tannin, boric acid, caprolactam, hexamine	2:5:2:1	6
17	Tannin, boric acid, caprolactam, hexamine, sodium hydroxide	2:5:2:1:0.08	9
18	Tannin, boric acid, caprolactam, hexamine, sodium hydroxide	2:5:2:1:0.02	7

Note: “nd”-not determined.

4.2.3 Fourier Transform-Infrared Spectroscopy (FT-IR) analyses

A PerkinElmer Frontier FT-IR spectrometer (PerkinElmer, Inc., Waltham, MA, USA) equipped with DTGS detector and a 9-bounce MIRacle™ diamond horizontal ATR element (PIKE technologies, Madison, WI, USA) was used for all of the experiments (Figure 4-1). For each measurement 32 interferograms were co-added spectrum and Fourier transformed at a spectral resolution of 2 cm^{-1} in the 4000 to 500 cm^{-1} range. Dry air purge was maintained during all data acquisition. All absorbance spectra were recorded at room temperature and analyzed using Spectrum 10™ software.

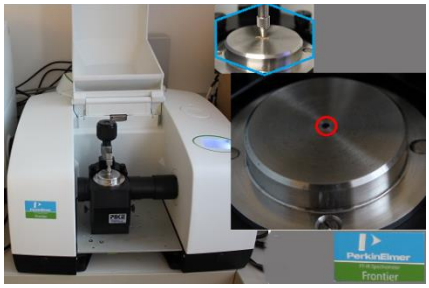


Figure 4-1 PerkinElmer Frontier FT-IR spectrometer

A background spectrum of air was scanned before each series of measurements. The background spectrum was recorded on using the same number of scans, resolution and

wavenumbers interval as the sample spectra. The same procedure was used for scanning blank spectra. Blanks were scanned before and after the analysis of each sample in order to be able to correct non-specific changes in the sample spectra and to assess the ATR crystal cleanliness for avoiding cross-contamination. The ATR crystal was carefully cleaned between samples with anhydrous ethanol. The cleaned crystal was checked spectrally to ensure that no residue from the previous sample was retained on the crystal surface. The polymer powder was pressed against the diamond crystal of the ATR device. A pressure applicator with a torque knob ensured that the same pressure was applied for all measurements. Both, sample and blank spectra were obtained in the absorbance mode. Each polymer sample was analyzed in duplicate, with each replicate acquired on a different day. Two spectra were obtained for each sample and the average spectra were reported.

4.2.4 ^{13}C Nuclear Magnetic Resonance (NMR) analyses

The samples for the ^{13}C NMR analysis were prepared by mixing deuterated methanol and aforementioned polymers. The liquid ^{13}C NMR spectrum of this solution was obtained on a Brüker Ascend™ 500 spectrometer (Figure 4-2, Bruker, Rheinstetten, Germany) at 25 ℃. The spectra were taken at 62.90 MHz for a number of transients of approximately 1000 and run with a relaxation delay of 5 s. Chemical shifts are expressed in parts per million (ppm) relative to the deuterated trimethylsilyl propionic acid (TSP-d4) as internal standard. Each sample was analyzed once.

Figure 4-2 Brüker Ascend™ 500 spectrometer

4.2.5 Impregnation scheme

Samples were oven-dried at 103 ℃ until constant weight (M_0). All treatments were performed using a single vacuum pressure impregnation: 30 min at 8mbar in a treatment desiccator, introduction of the treatment solution in the desiccator, pressure slowly increased up to ambient pressure, the specimens were kept in the tannin-based solution for 24 hours (Figure 4-3). After the impregnation treatment, the excess solution of specimen surface was removed with a blotting paper; and the weights of the treated humid wood blocks were recorded (M_1).

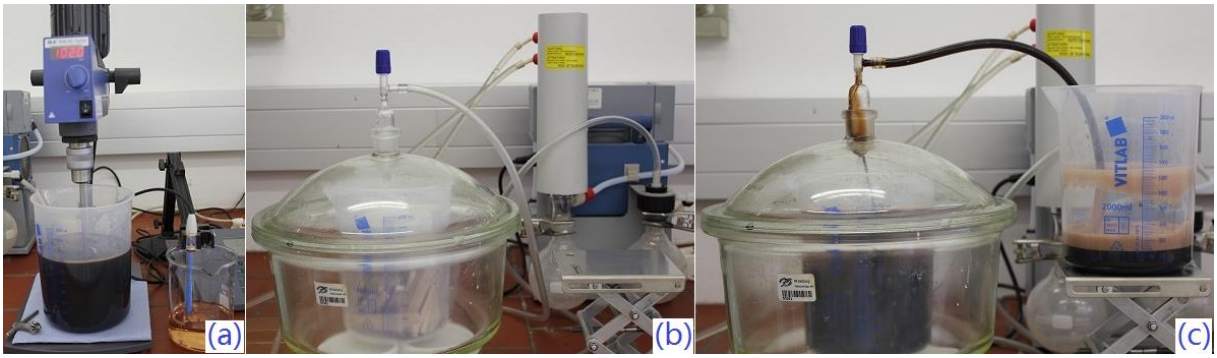


Figure 4-3 Impregnation scheme: a-preparing impregnation solution, b-performing an 8 mbar vacuum and c-slowly impregnating tannin-based preservative

The retention of the products was calculated according to equation (4-1):

$$R = \frac{(M_1 - M_0) \times C}{V} \quad (4\text{-}1)$$

where R (kg/m^3) is the retention of impregnation material, "M_1-M_0" is the kilograms of treating solution absorbed by the sample, C is the concentration (%, w/w), and V is the volume of the samples (m^3).

The treated samples were cured at 103 ℃ for 12 hours to allow polymerization of the products. Their weight (M_2) was recorded after curing.

4.2.5.1 Impregnation solution for laboratory biological and fire tests

For each treatment solution at least 72 samples were treated.

The impregnation solutions were a mix of the following aqueous solutions (% w/w): mimosa extract (10%), NaOH (50%), hexamine (33%), boric acid (5%), ε-caprolactam (40%) or polyethylene glycol 400 (PEG, 20%). The concentration of each ingredient of the formulation is presented in table 4-2. The pH of these solutions was always corrected with NaOH 50% to a pH value of 9.0.

PEG was also used as an additive to make the polymer network more flexible. The treatment methods are exactly the same as described earlier, and the work is reported here for comparison (Tondi et al., 2015)

Table 4-2 Advanced tannin-boron formulations

Additive / Formulation	Tannin (%)	Boric Acid (%)	Hexamine (%)	NaOH (%)	PEG (%)	Caprolactam (%)	Water (%)
Free Boric Acid	-	0.43	-	-	-	-	99.57
Tannin-Boron	9.73	0.49	0.58	0.49	-	-	88.72
PEG-Tannin-Boron	9.72	0.49	0.58	0.49	19.41	-	69.34
ε-Caprolactam-Tannin-boron	8.14	0.41	0.49	0.41	-	15.56	75.01

4.2.5.2 Impregnation solution for unsterile soil-bed tests

Seven series of 100 samples were impregnated with different tannin-boron formulations (table 4-3). The formulations of the treatment solutions have been adjusted for the unsterile soil-bed tests as the fungi toxic threshold for boron compounds is higher in ground contact (Drysdale, 1994). A wider range of concentration was used in order to eventually obtain a dose/response effect. After curing, the samples were stored in a climatic chamber at 20 ℃ and 65% RH.

Table 4-3 Advanced tannin-boron formulations for unsterile soil-bed tests (% w/w)

Formulation	Tannin	Boric acid	ε-Caprolactam	Hexamine	pH
F-1	15%	0	13.1%	0.9%	9
F-2	15%	1%	13.1%	0.9%	9
F-3	15%	1.5%	13.1%	0.9%	9
F-4	15%	2%	13.1%	0.9%	9
F-5	15%	2%	13.1%	0.9%	4.75
F-6	15%	2.5%	13.1%	0.9%	9
F-7	15%	3%	13.1%	0.9%	9

4.2.6 Colour measurement

The colour of the treated and untreated specimens was measured with a Mercury 2000 spectrophotometer (Datacolor, Lawrenceville, NJ, USA) under a D_{65} light source and an observer angle of 10 °(A_{10}). The sensor head of the spectrophotometer was 11 mm in diameter. The CIELAB colour space was characterized by three parameters L*, a*, and b*, which respectively represent the lightness of the colour (L* = 0, black and L* = 100, white), its position between red (+a*) and green (-a*) and its position between yellow (+b*) and blue (-b*).

Three specimens, randomly chosen in the controls and treated samples, were used in each case. It has to be specified that the samples used always have a proportion of latewood below 30% (as required in the biological tests standards). For each specimen, 3 measurements were done on one tangential face.

4.2.7 Leaching and boron analysis procedures

The boron leaching of the specimens was performed according to ENV 1250-2(1995) and EN 84 (1997) (Figure 4-4).

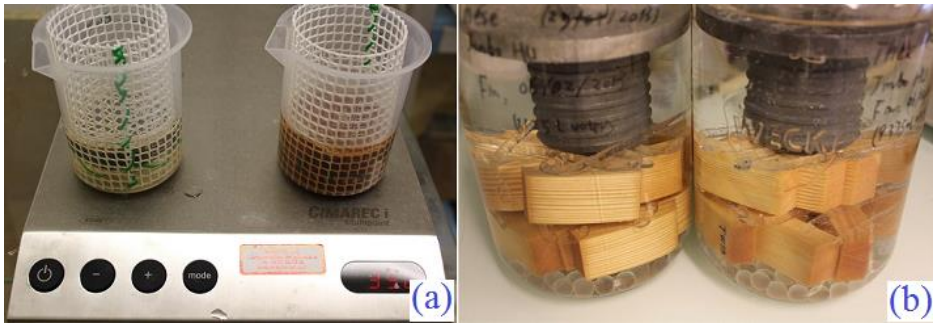


Figure 4-4 Leaching schemes of samples: (a) presents ENV1250-2 and (b) represents EN84

The leaching according to ENV 1250-2 was as follow: two series of six samples were immersed in 600 mL deionized water (1 vol. wood/5 vol. water) and subjected for six leaching periods of increasing duration under continuous stirring at 20 ℃ and 65% RH. Water was replaced for each leaching period after 1 h, 2 h, 4 h, 8 h, 16 h and 48 h. All leachates were collected and kept at 4 ℃ for leached boron or tannin analysis.

The analysis of boron was performed for the ENV 1250-2 leachates only.

The aqueous leachates from the treated samples were performed with an Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) to determine the concentration of boron. The solutions were nebulized in a chamber with cyclonic double pass and the AES was set for detecting the emission at the wavelength of 249.7 nm with a read and stabilization time of 3 and 20 s respectively.

The collected boron concentration allowed calculating the degree of boron fixation which was calculated according to following equation:

$$B_r(\%) = \frac{B_0 - B_1}{B_0} \times 100\% \quad (4\text{-}2)$$

where $B_{(r)}$ is the boron degree of fixation (%); B_0 is the average uptake of boron and potential amount of leachable boron (kg/m^3); B_1 is the leached out boron in solution related to the amount of wood (kg/m^3).

The percentage reduction of boron in the specimens was calculated based on the initial amount of boron in the specimens. The percentage of the leached tannin was determined as:
The second leaching process was done according to EN 84: two series of six samples were fixed into containers and submerged into water (1 volume wood / 5 volume water) under a 4-kPa vacuum for 20 min, and left for 2 hours. The water was changed after 2 hours, and nine times on alternate days during a period of 14 days.
After the leaching, wood specimens were conditioned at 20 ℃ and 65% RH until they reached constant mass.

4.2.8 Laboratory decay resistance test

A mono culture decay test was conducted according to EN 113 (1996) using a brown-rot fungus *Antrodia spp*. (tropical strain CTFT 57A). Sterile culture medium (65 ml), prepared from malt (40 g) and agar (20 g) in distilled water (1 liter), was placed in a culture flask, inoculated with a small piece of freshly grown pure mycelium and incubated for 2 weeks to allow full colonization of the medium by the mycelium. Leached and unleached treated samples, as well as control samples were sterilized by gamma radiation prior to biological testing. Two blocks (one treated and one control, 6 replicates) were placed on a sterile support on malt agar medium in each culture (Figure 4-5) flask under sterile conditions. Incubation of *Antrodia spp*. was carried out at 27 ℃, 75% HR in a climatic chamber for 16 weeks. Once the fungal exposure was finished, the blocks were removed from the test bottles, and the mycelium was carefully brushed off the samples, the samples were weighted (humid mass, M_3) were then dried at 103 ℃ and weighed (M_4). Six controls of untreated pine sapwood samples were used to check the virulence of the fungus.

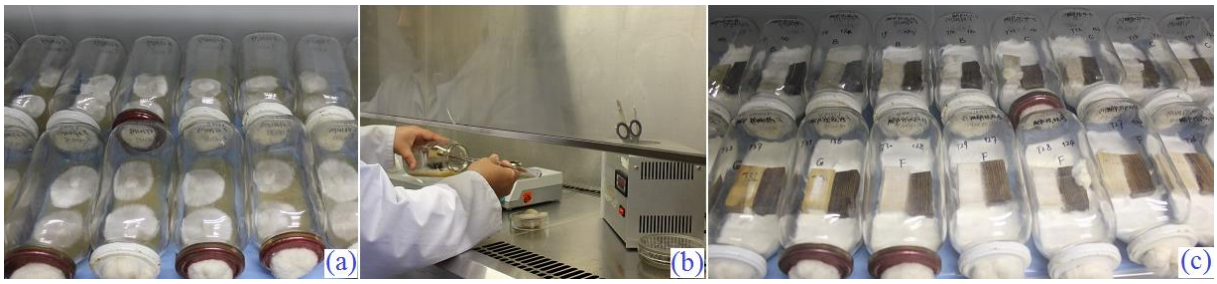


Figure 4-5 Fungus test: a-incubating fungi, b-arranging the samples on fungi colonized medium and c-incubation

The humidity at the end of the test was determined according to equation (4-3):

$$M_H = \frac{M_3 - M_4}{M_3} \times 100\% \quad (4\text{-}3)$$

where M_H (%) is the moisture at the end of biological test. M_3 and M_4 have been signed in the aforesaid content (g).
The extent of the fungal attack was determined based on the percentage of weight loss. Weight loss (W_L, %) was expressed as a percentage of the initial oven dried weight of the sample according to the formula (4-4):

$$W_L = \frac{M_2 - M_4}{M_2} \times 100\% \quad (4\text{-}4)$$

where M_2 and M_4 were the initial and final dried mass (g) of the samples before and after exposure to fungus respectively.

Identical pine sapwood samples were treated in the batch of treatment solutions. Half of them were leached, and were tested for their resistance against *Coniophora puteana* according to EN113. The methodology is the same as described above. Part of this work was performed by G. Tondi and S. Palanti at Ivalsa, CNR, Italy, and was presented here for comparison.

4.2.9 Termite bioassay according to EN 117

Termite assays referred to "3.2.5 Laboratory no-choice termite EN117 methodology".

4.2.10 Short-time exposure lab-scale fire tests

Scots pine sapwood samples of dimensions 50×25×15 mm^3 (L, R, T) were treated with the solution containing caprolactam (table 4-2), as described in §4.2.6. 9 samples were treated and separated into 3 lots: unleached, leached according to ENV 1250-2 and EN84.
Once the biological tests against *Antrodia* (EN113) and termites (EN117) were done, the samples treated with the solution containing ε-caprolactam, were re-conditioned at 20 ℃, 65% RH until constant weight was reached. Three samples of each biological test (unleached and leached) were taken randomly and tested against fire (Tondi et al. 2012). The larger surface of each sample was exposed to the 100% oxidant flame of a Bunsen burner (Figure 4-6). The distance between Bunsen burner and sample was set at 9 cm and the burning times were controlled with a stop-watch. Ignition, flame and ember time were recorded for each sample. The ignition time was the minimum exposure time necessary to activate unaided burning. The flame time measures the time that the sample requires to extinguish the flame after 2 minutes of continued exposure. Ember time measures the time required for complete extinction (no more red spots, no more fumes).

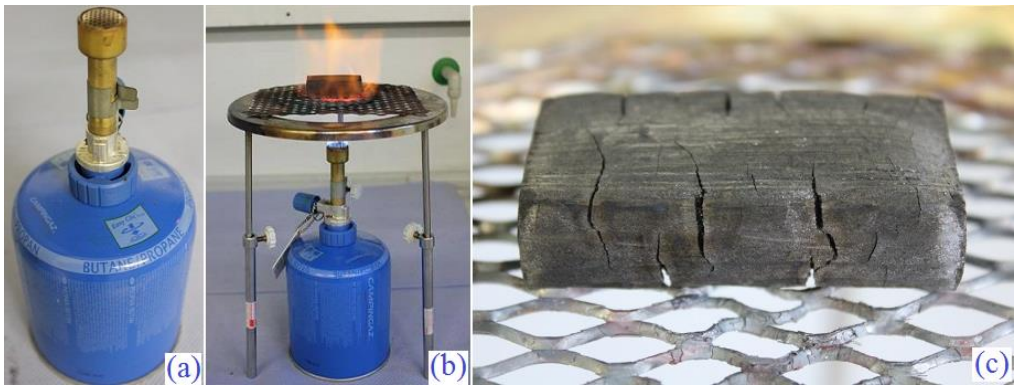


Figure 4-6 Short-time exposure fire test by a simplified lab-scale apparatus: a-a burner, b-a short-time exposure fire test and c-a specimen after the 2-minute combustion

4.2.11 Bending tests

Treated and untreated specimens (100×10×5 mm^3) were tested for their mechanical properties with a Zwick/Roell Z250 universal testing machine at a crosshead speed of 2 mm/min. Six samples from each series of boron concentration were measured with a static 3-point bending test (span - 80 mm) (Figure 4-7). The test results including ultimate modulus of elasticity (MOE) and modulus of rupture (MOR), which represents the area under the stress-strain curve, were obtained via the software (testXpert 2). The

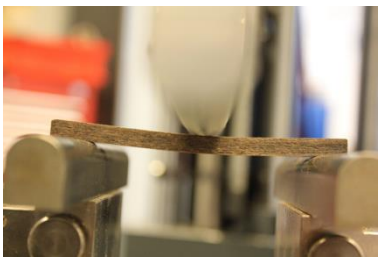


Figure 4-7 Treated specimen in machine for bending test

thickness, width and length of the test specimens were measured prior to testing by a digital micrometer.

4.2.12 Unsterile soil-bed tests

Unsterile soil-bed test were performed according to the guidelines of ENV807 (2001).
The 100×10×5 mm^3 treated and control specimens were buried to 20mm of their length protruding above the surface of the soil and with a minimum of 20mm between adjacent specimens and from the sides of containers, filled with soils. Three soils were taken from 3 test sites: Montpellier (France), Kourou (French Guiana) and Changsha (China) (Figure 4-8). In each test container was added a recorded quantity of soil was humidified (depending on its water holding capacity). The ground-contact tests in Changsha and Kourou were performed at ambient temperature and relative humidity (test container outside, protected from the rain), the tests in Montpellier were performed at 27 ℃, 75% RH in a climatic room.

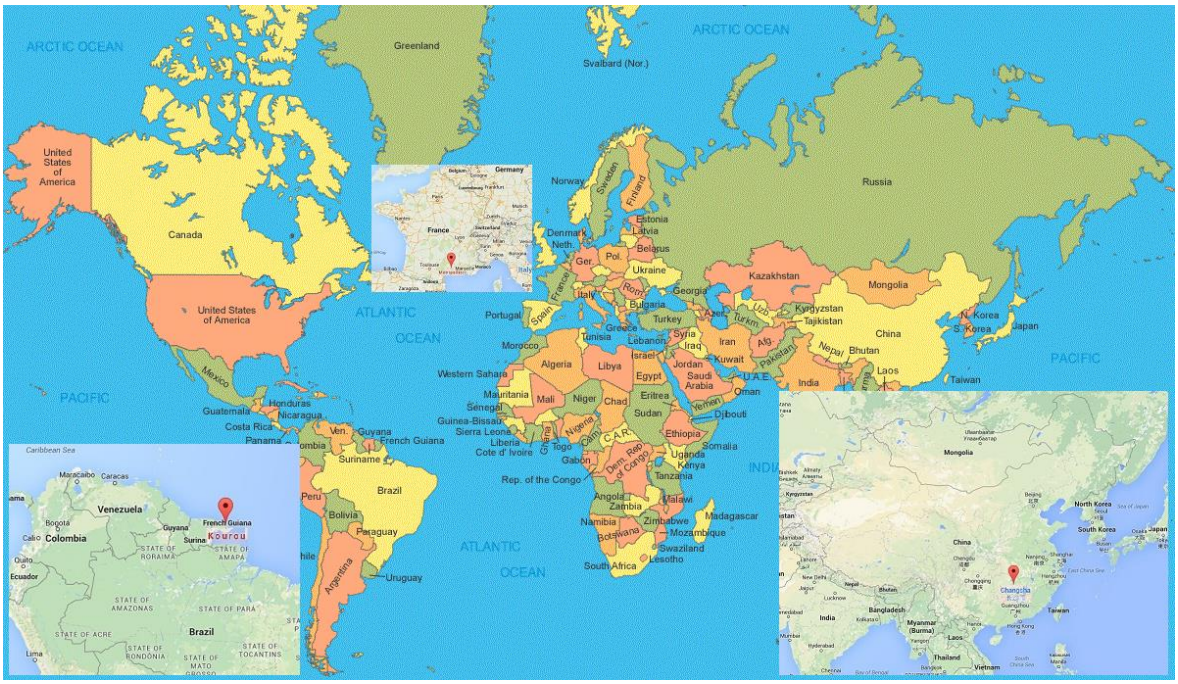
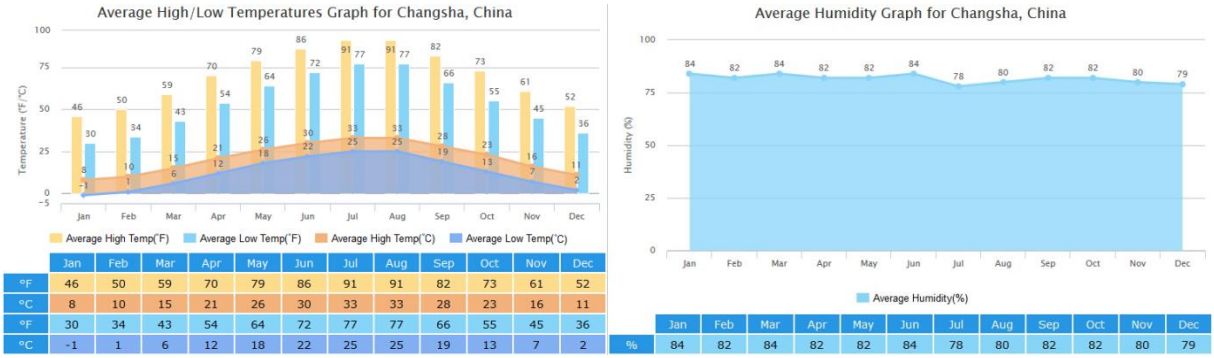


Figure 4-8 The geographical layout of field test

Changsha is located in the region with continental subtropical seasonal humid climate. It has four distinct seasons, abundant sun, long frostless periods and abundant rain. The average temperature in Changsha is between 16 ℃-18 ℃, and then the average humidity in Changsha is 78%-84% (Figure 4-9).



	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
°F	46	50	59	70	79	86	91	91	82	73	61	52
°C	8	10	15	21	26	30	33	33	28	23	16	11
°F	30	34	43	54	64	72	77	77	66	55	45	36
°C	-1	1	6	12	18	22	25	25	19	13	7	2

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
%	84	82	84	82	82	84	78	80	82	82	80	79

Figure 4-9 Average temperature and humidity in Changsha (http://www.chinahighlights.com)

Six replicates of each series were tested in each of three widely geographically separated lab-plots to ensure exposure to different type terrestrial microcosms. All test specimens were randomly assigned to boxes (Figure 4-10). Untreated controls were pine, beech, simarouba and African padauk. After a fungal exposure of 3, 6, 10 and 12 months, 6 stakes of each series were removed and cleaned from adhering soil by a brush. And they were recorded their humidity weights. They were weighed again after drying 24h at 103 ℃. The humidity at the end of the test (Eq. 4-3) and the mass loss due to soil exposure (Eq. 4-4) were calculated. The field tests in French Guiana are still running and will not be presented here.

Figure 4-10 Sample arrangements in (a)-Montpellier, (b)-French Guiana and (c)-Changsha

4.3 Results

4.3.1 Chemical mechanism of tannin-boron-ε-caprolactam formulation

In order to elucidate the chemical reactions mechanism, mixtures of tannin, boric acid, hexamine and ε-caprolactam, have been investigated using ATR FT-IR spectroscopy.

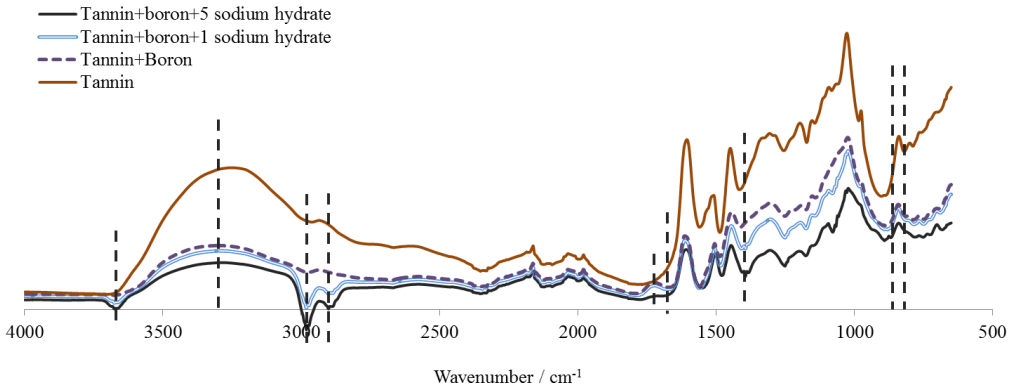


Figure 4-11 FTIR spectra of tannin and samples obtained tannin-boron systems at several pH

Previous studies had proved that polyflavonoid tannins can autocondense and harden when in presence of boric acid (Meikleham et al. 1994, Pizzi et al. 1995, Pizzi and Meikleham 1995). The FTIR analysis of tannin and tannin-boron at different pH value was shown in Figure 4-11. The broad peak in the region 3200-3500 cm^{-1} was characteristic of the –OH stretching of the benzene nucleus and of the methylol group of tannin. The small peak around 3670 cm^{-1} was due to free hydroxyl groups of B–OH stretching vibrations. The region between 2900 and 3000 was typical of C-H stretching vibrations: the one at 2900 cm^{-1} was C-H aliphatic, while another one at 3000 cm^{-1} was C-H of aromatic rings (The spectra containing NaOH in figure 4-11 presented wrong mathematic transformation because the two valleys should be two peaks when the spectra was observed in absorbance). The signal of 1720 cm^{-1} was typical for C=O stretching absorption, of which intensity was increased after adding boric acid maybe

due to boron containing mixtures in presence of sodium. The B–O stretching vibrations were observed in the region of 1500 - 1100 cm^{-1} and, significant changes were observed in these bands by the fixation of boron in the tannin polymer; especially, the small peak 1392 cm^{-1} probably due to –CH bending vibration abruptly decreased after increasing pH value. The O–B–O bonds were inspected between 700 and 900 cm^{-1}, because of the specific affinity and complex formation between boron and some phenolic groups of tannin resin (Erdem et al. 2012).

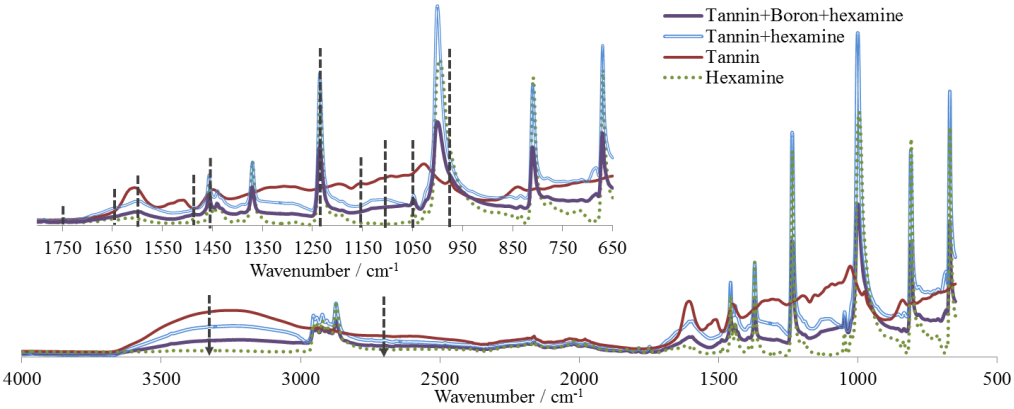


Figure 4-12 FTIR spectra of hexamine, tannin and samples obtained tannin-hexamine and tannin-boron-hexamine systems

From the analysis of the spectra (Figure 4-12), CH Bending arom asymmetric of tannin at 1500 and 1450 cm^{-1} (Tondi and Petutschnigg 2014) disappeared after tannin-based polymerization. Likewise, bands at 1150 and 960 cm^{-1}, due to the C–O groups of resorcinol-like molecules of tannin, were reduced after the reaction among tannin, boric acid and hexamine. The broad peak in the region 3000–3700 cm^{-1} of tannin resins was characteristic of the aromatic –OH stretching and of the methylol group of activated tannin. The small peaks in the region between 3000 and 2800 were associated to aliphatic and aromatic C-H stretching of the benzene nucleus, methylene and dimethylene ether bridges of the tannin-based resin. The signal at 1600 cm^{-1} is characteristic of the aromatic C–C stretching. Thus, 1235 cm^{-1} band can be attributed to the antisymmetric deformation of C–O–C in ether groups. Other bands at 1110, 1030 cm^{-1} can be attributed to presence of C–N groups (Pena et al. 2009). There were two new bands at 1645 and 1740 cm^{-1} probably due to the formation of azomethine groups (Aranguren et al. 1982, Pichelin et al. 1999) and to the formation of ester groups, respectively.

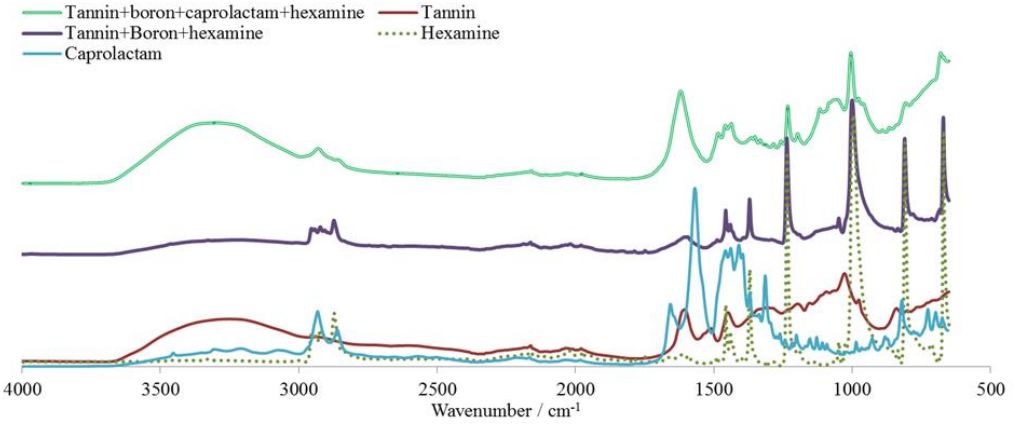


Figure 4-13 FTIR spectra of hexamine, tannin, caprolactam and samples obtained tannin-boron-hexamine and tannin-boron-caprolactam-hexamine systems

Figure 4-13 showed ATR-FTIR spectra for hexamine, tannin, caprolactam and polymers obtained tannin-boron-hexamine and tannin-boron-caprolactam-hexamine systems. For tannin-boron-caprolactam-hexamine polymer, three typical amide of polycaprolactam at about 3300 cm^{-1} N–H band, 1660 cm^{-1} C=O band and 1570 cm^{-1} C–N band disappeared after the polymer reaction. This polymer presented 1620 cm^{-1} corresponding to carbonyl stretching vibrations of the caprolactam ring, which overlaps with stretching carbon-carbon vibrations of aromatic rings of tannin. The bands at 1443, 1463 and 1481cm^{-1} were recognized $–CH_2$ scissors vibration. Other peaks also appeared in the spectrum of tannin-caprolactam polymer: for the CO–NH group at 1190 cm^{-1}, N–H bending at 1264 cm^{-1}, $–CH_2$ sequences at 1391 cm^{-1}, 2858 and 2928 cm^{-1} (antisymmetric and symmetric $–CH_2$–stretching) (Erel-Unal and Sukhishvili 2008, Rusu et al. 2009, Kharlampieva et al. 2005).

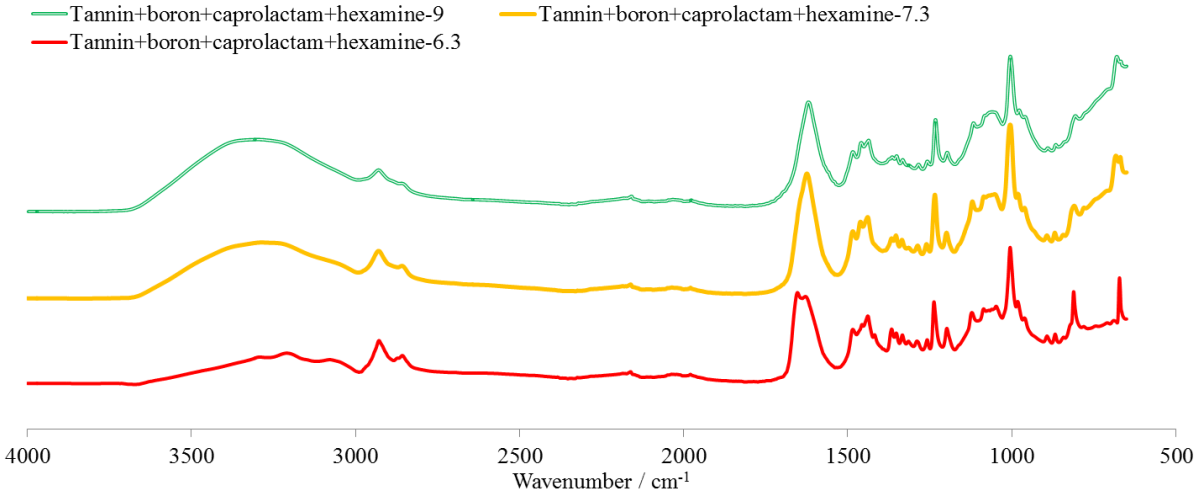


Figure 4-14 FTIR spectra of samples obtained tannin-boron-caprolactam-hexamine systems at different pH levels

Figure 4-14 illustrated the spectrum of tannin-caprolactam polymer at various pH values. This polymer in weak acid environment was different with others band at region of 3000-3500 cm^{-1} and 1500-1700 cm^{-1}. The signals at around 3300 cm^{-1} assumed a broader shape increasing the pH because the –OH groups increased their mobility due to external addition of NaOH. The shoulder at around 1700 cm^{-1} can be the C=O stretching of increasing caprolactam, while the pH decreased because of the ring opening and consequent formation of polymers in which the C=O shifted to slightly lower wavenumbers and overlapped with the aromatic C=C stretching. ^{13}C-NMR spectra were applied in this study in order to progressively understand some chemical modification occurred in tannin during activation. When liquid-phase ^{13}C-NMR was run, only solubilized samples can be seen that the signals of the fraction were dissolved in deuterated methanol and deuterium oxide in this study. Thus, these fractions could not allow finding any new band, because the polymers were usually insoluble in most of the common solvents. Then, in this case, the presence of very low signals due to tannin as soon as the polymer taken place, could mean that the tannin oligomers had been almost always fully crosslinked while the hardeners (hexamine and maybe caprolactam) were visibly detected because of the excess of them been soluble in the solvents.

Figure of ^{13}C-NMR spectra in the Annex D, solid ^{13}C-NMR of polymer sample N^{o} 2, 3, 5, 6, 7, 11, 12, 13, 14, 15, 16, 17 and 18 did not present new chemical information.

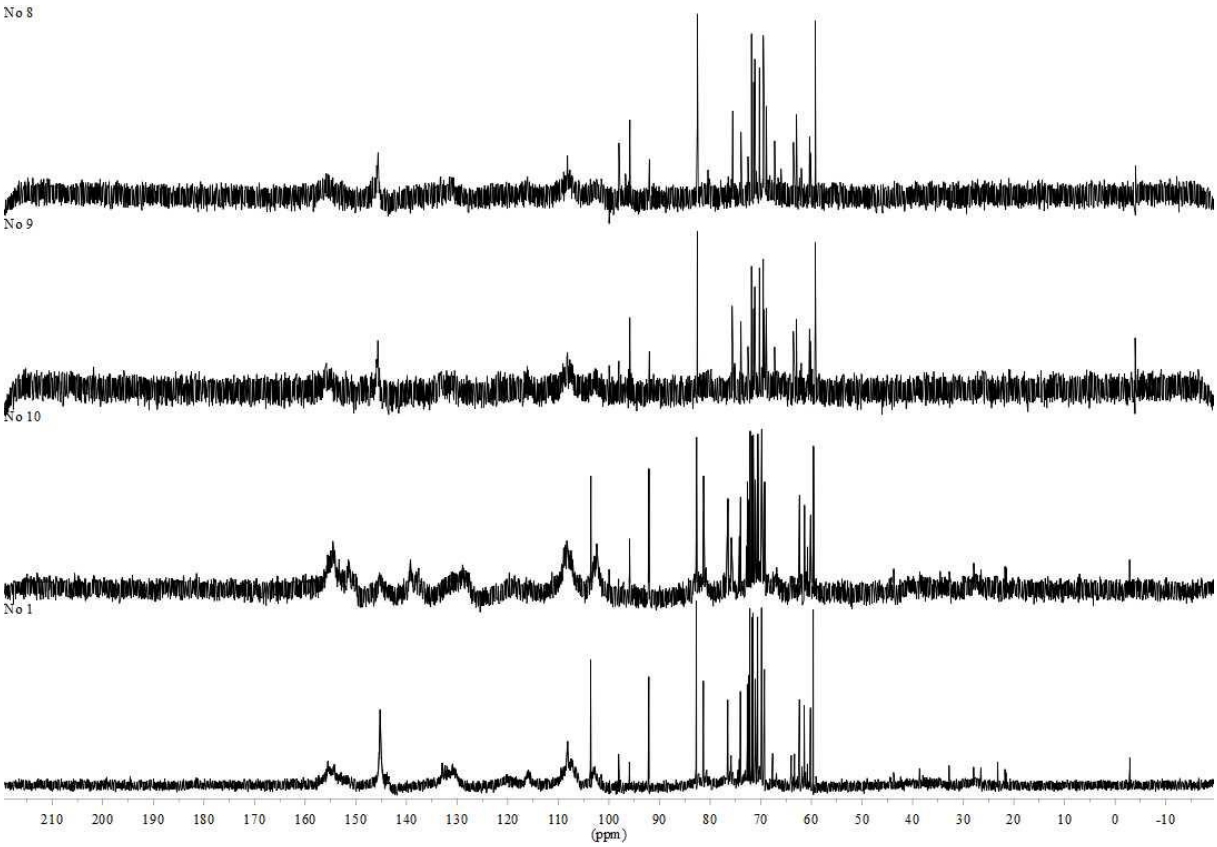


Figure 4-15 ^{13}C-NMR of tannin and tannin-boron resin at different pH levels

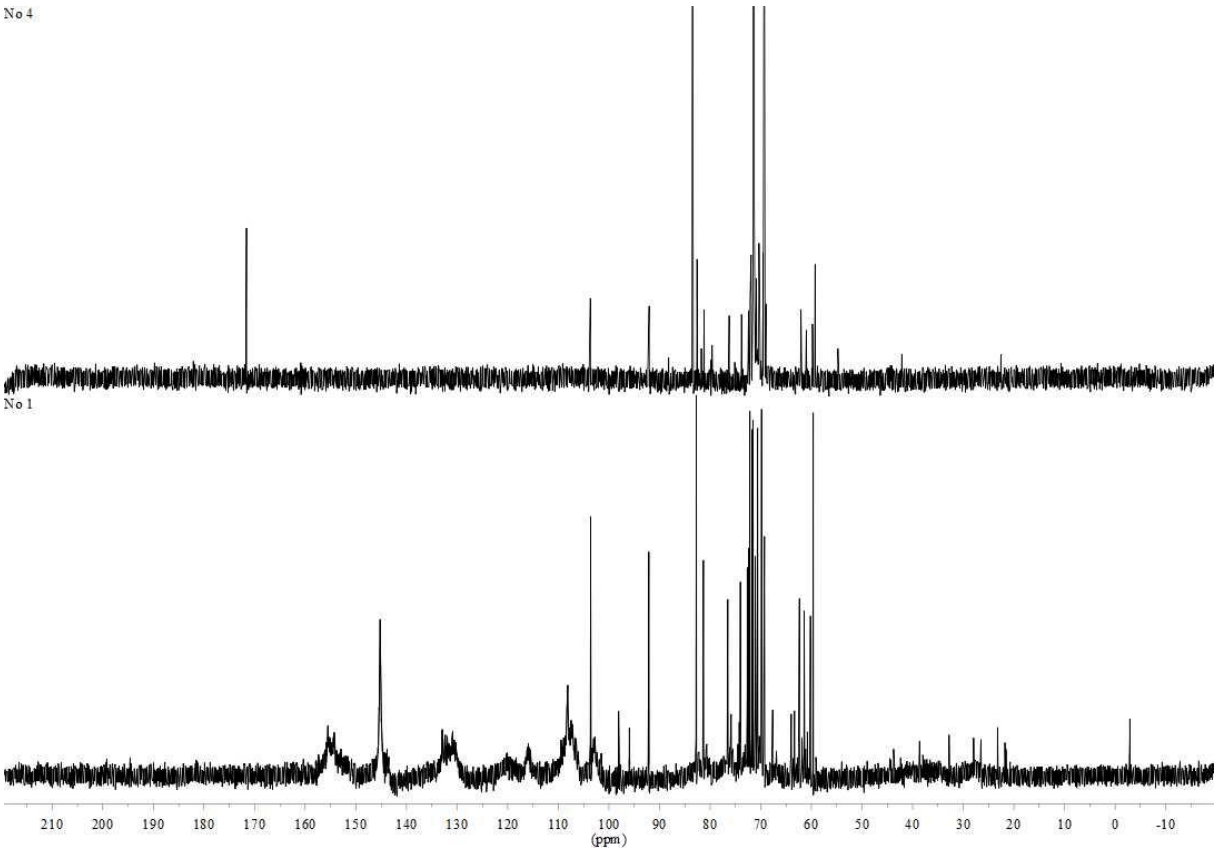


Figure 4-16 ^{13}C-NMR of tannin and tannin-hexamine resin

The spectrum of N° 1 was representing tannin only. Considering the pure products (N° 2 and 11) the signal at 72 ppm was CH_2 of hexamine, while that at 182, 42, 35, 30, 28 and 22 were the 6 carbon atoms of ε-caprolactam (N° 3 and 12). In the spectrum N° 3 there was other signal than only caprolactam. Most of them can be attributed to 6-amino hexanoic acid that was nothing else than the caprolactam opened in the amidic bond. With comparison to the spectra of N° 1 and 2, the two new signals at 83 and 56 ppm in the spectra of No 4 were separately CH_2–OH and NH_2–R groups. The spectra of N° 5 looked like pure ε-caprolactam. The spectra of N° 6 did not show signal of caprolactam, as well as, the tannin signals were too small to be interpreted or find new signals. The spectra of N° cannot confirm the new signals of the spectra of N° 4, and signals were so small that no interpretation was really possible. The spectra of N° 8 and 9 were registered with lower acquisition time than the spectra of N° 1. No comparison was possible because the differences were not effective. The spectra of N° 10 even if registered with lower resolution allowed observing a new signal at 139 ppm (comparing with the spectra of N° 1). This was in the region of acid/aromatics. It meant that the covalent adduct between boric acid and the tannin molecules cannot be excluded. However the low resolution did not really allow to be sure. The spectra of N° 13 had again the signals of tannin too small and no interpretation was really possible. The spectra of N° 15 presented all the peaks expected and also a lot of other smaller signals. The spectra of N° 16, 17 and 18 again presented a very weak signal set of tannins and nothing was really visible.
With comparison to N° 1, N° 8 and N° 9 samples, the spectrum of N° 10 can be inspected a new signal at 139 ppm, due to the effect of NaOH and boric acid (Figure 4-15).
Possibly, the most important observation can be done in N° 4 sample: 170 ppm, 56 and 83 ppm (Figure 4-16). These signals could be due to the activation of tannin.
Unfortunately, only a limited amount of information was collectable due to the very limited amount of signal because the more the of polymer crosslinked, the less it was soluble in CD_3OD.

4.3.2 Retention of treated wood

The retention levels of two sets of samples treated with advanced tannin-boron formulation were respectively reported in the following table 4-4 and 4-5.

Table 4-4 Retention of 50×25×15 mm^3 samples for the different tannin-based formulations

Formulation	Total (SD) kg/m^3	Tannin (SD) kg/m^3	Boron (SD) kg/m^3
Free Boric Acid	3.14(0.08)	0	3.14(0.08)
Tannin-Boron	402.06(5.07)	76.70 (0.81)	3.86(0.04)
PEG-Tannin-Boron	1048.36(24.17)	75.68(1.37)	3.82(0.07)
ε-Caprolactam-Tannin-boron	665.60(15.03)	62.86(1.28)	3.17(0.06)

Significantly highest liquid retention was registered when tannin/boric acid/PEG solutions were applied, due to the thick outside layer of PEG (Tondi et al., 2015). The presence of PEG did not really modify the retention of tannin and boric acid, compared to tannin-boron formulation. The formulations containing caprolactam showed a lower retention than tannin-

boron solution, but almost no difference in boron uptake when compared with boric acid alone.

Comparing the retention of the solution with caprolactam (Tables 4-4, 0.41% boric acid) and solution F2 (table 4-5, 1% boric acid), it appears that the boron retention for F2 is almost doubled in the Pine samples, indicating that there is no effect of the sample geometry. The beech samples (table 4-5) show a linear uptake of boron along with the increasing concentration of boron for F2 to F4 and F5 solutions. For higher concentrations of the solution, this uptake does not remain proportional. Pine samples showed highest variations in the uptake of active ingredients as already noticed by Tondi et al. (2013b).

Table 4-5 Retention of 100×10×5 mm^3 sample in the ε-Cap-Tannin-boron formulation

Additive and wood species		Retention in different formulation						
		F-1	F-2	F-3	F-4	F-5	F-6	F-7
Total (SD) kg/m^3	Pine	123.40 (7.87)	203.31 (12.25)	232.18 (12.72)	270.42 (11.00)	264.23 (12.10)	252.40 (7.57)	224.68 (13.49)
	Beech	124.05 (3.13)	260.28 (6.50)	270.57 (8.40)	278.67 (7.07)	265.61 (4.53)	277.25 (4.79)	284.62 (4.39)
Tan. (SD) kg/m^3	Pine	123.40 (7.87)	98.38 (9.67)	108.83 (6.95)	122.92 (5.00)	121.95 (5.59)	110.32 (9.82)	93.61 (5.62)
	Beech	124.05 (3.13)	125.94 (3.14)	126.83 (3.94)	126.67 (3.21)	122.92 (2.09)	120.54 (2.08)	118.59 (1.83)
BA (SD) kg/m^3	Pine	0	6.56 (0.58)	10.88 (1.22)	16.39 (0.67)	16.26 (0.74)	18.39 (1.64)	18.72 (1.13)
	Beech	0	8.40 (0.20)	12.69 (0.39)	16.89 (0.43)	16.77 (0.28)	20.09 (0.35)	23.72 (0.37)

The sodium hydroxide was added as a pH-adjusting factor of tannin polymer did significantly not influence the retentions of tannin and boric acid (solutions F4 and F5).

4.3.3 Visual evaluation after the treatment

Tannin-based water-borne solutions have always a brownish color. In particular, when the pH turns to alkaline, the flavonoids assume an even darker color that tends to black for highly concentrated solutions. Also the advanced formulation containing ε-caprolactam does not differ from the original tannin-based formulations (Figure 4-17).

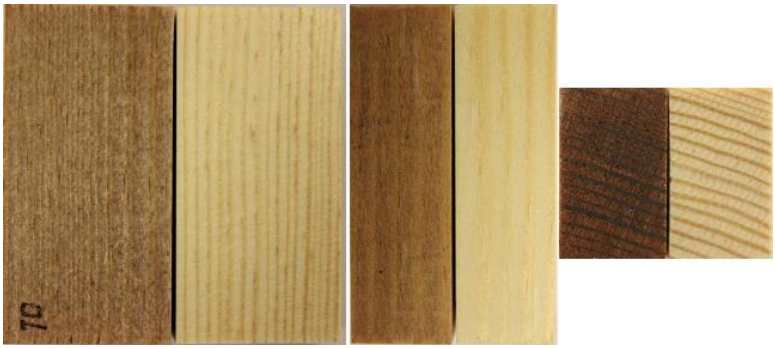


Figure 4-17. Colour change of treated and untreated pine wood samples, from left to right, radial, tangential and transverse section

It can be observed that the treated samples show an overall colour change (figure 4-18). The lightness *L** is considerably decreased (darker colour), as well as *b** to a lesser extend (bluer colour). Even if slightly increased (small shift to the red), *a** is the less affected parameter.

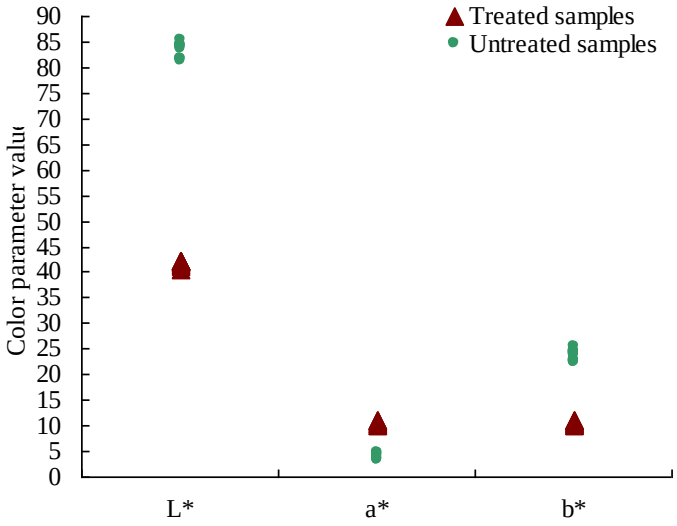


Figure 4-18. Colorimeter assessment of treated (tannin-boron-caprolactam) and untreated pine wood samples

4.3.4 Boron leaching after ENV 1250-2 leaching test

One of the most important aspects to be monitored for the advanced tannin-based wood preservatives is their behavior against boron leaching. It was previously observed (Tondi et al., 2012) that the network of tannin was able to considerably protect the boron from leaching. For this reason the introduction of new substances in the formulation does ensure that the polymerization maintains the fixation of boron during leaching.

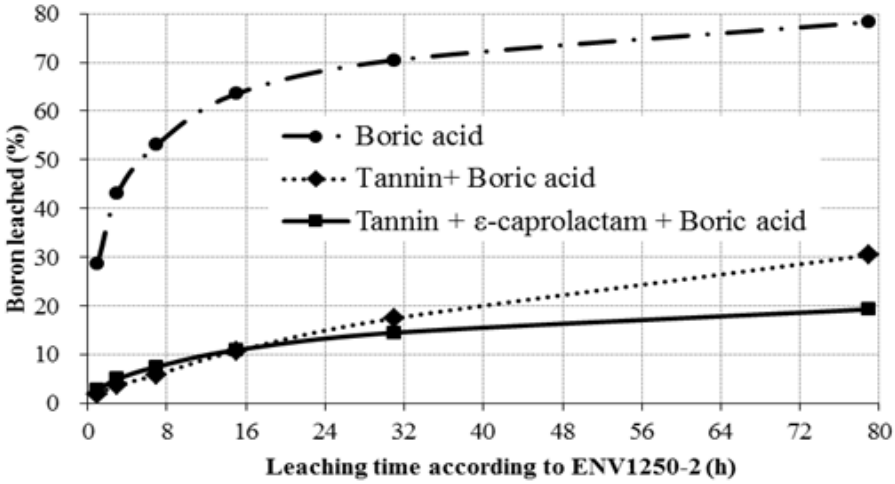


Figure 4-19. Amount of boron leached for pine sample treated with advanced tannin-boron wood preservative in comparison with the original formulation (20% tannin, 1% boron) and a water solution of boric acid

The percentage of boron leached during the ENV 1250-2 test is reported in figure 4-19.
The graphic reported in figure 4-19 shows that the presence of tannin network significantly hinders the leaching of boron. In particular, the formulation containing ε-caprolactam fixes the boron around 50% better than the classical tannin-based wood preservatives.

This observation suggests that the polymerization of tannin and hexamine includes actively the ε-caprolactam in the network and the boron fixation results even enhanced. These results underline that the tannin-boron treatments modified with ε-caprolactam may supply lasting protection against wood degradation in outdoor exposures.

4.3.5 Biosusceptibility to no-choice laboratory tests (EN113)

In the figure 4-20 and Annex E the weight loss of the unleached and leached specimens exposed to *Antrodia* are reported.

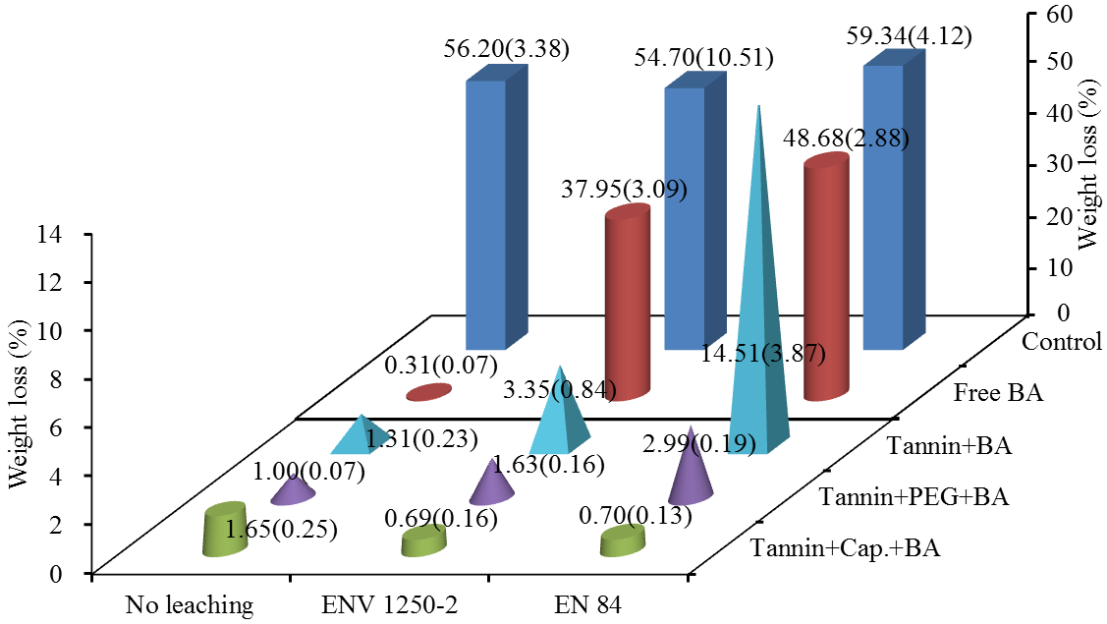


Figure 4-20 Average weight loss (Standard deviation) of treated and untreated Scots pine samples during the decay tests against *Antrodia*

For all unleached samples, the presence of boron guarantee optimal results for each of the formulation studied. Moreover, in the wood samples treated with tannin formulation containing, the efficacy is lower because some of the boron atoms are with high probability covalently linked with the network and therefore, the activity is slightly lower (Tondi et al. 2012b). On the other hand, biological tests always present some variability. Thus, from a biological point of view, all the formulations tested (including free boric acid) are classified as efficient against *Antrodia*.

As expected, boric acid alone does not provide any protection to the wood, when subjected to leaching. The efficacy of the tannin-containing formulations is very significant after leaching. For both of the leaching tests done, the formulations containing boron, offer much better performances than the formulations containing free boric acid. And particularly, the advanced formulations resist more than the classic tannin-based formulation especially when the leaching treatment applied is much stronger (EN 84).

All-in-all the advanced formulations containing ε-caprolactam-boron showed the highest resistance to *Antrodia* attacks even after the very aggressive EN84 leaching. Although figure 4-20 highlights the great efficacy of the tannin containing formulations and the tannin-PEG-boron treated blocks resisted decay after ENV 1250-2 leaching, the EN84 leached samples did not overcome the requirements of EN113.

Biological tests according to the EN113 have been done also exposing treated and untreated samples also against the most common *Coniophora Puteana*. The results of the test after 16 week of exposure are reported in table 4-6.

The results of the test highlight an abated mass loss for every specimen treated with tannin-boron formulations. Every formulation overcomes the requirement of the EN 113 except the classical formulation exposed to EN 84 leaching. In these experiments the lower biological aggressiveness of *Coniophora* is shown especially against the advanced formulations unleached. However, very weak weight loss was registered also after leaching.

Table 4-6 Behavior of the tannin treated samples against *Coniophora Puteana*

Formulation	Leaching norm	Boron content (%) Before leaching	Boron content (%) After leaching	Weight Loss (%)	Standard deviation
Control	Unleached	0.00	0.00	48.46	14.8
Free boron	Unleached	0.5	0.5	0.00	0.07
	EN 1250-2	0.5	0.3	11.48	0.81
	EN 84	0.5	0	54.47	0.12
Tannin-boron	Unleached	0.49	0.49	2.09	0.98
	EN 1250-2	0.49	0.34	0.64	0.46
	EN 84	0.49	0.32*	7.44	1.48
Tannin- boron-PEG	Unleached	0.49	0.49	0.00	0.33
	EN 1250-2	0.49	0.39*	0.47	0.49
Tannin-boron- ε-Caprolactam	Unleached	0.41	0.41	0.00	0.56
	EN 1250-2	0.41	0.33	0.48	0.03

*The values were only estimated on the basis of tannin leaching (ref Tondi).

The presence of PEG and ε-caprolactam gives best numerical results. However, it has to be noticed that the polyethylene glycol containing samples suffer a considerable mass loss (up to 7 grams) also for the reference sample exposed in the agar without fungal attack. This means that the polymer of PEG does not keep fixed in the structure of wood and that the fungi cannot easily get in contact with wood.

Another aspect to be considered is that the formulations containing ε-caprolactam have a high biologic resistance even if the current amount of boron is lower.

4.3.6 Biosusceptibility to no-choice termite

The enhancement of the biological resistance against brown-rot fungi does not always ensure the protection against the highly aggressive termites.

The termite resistance of untreated/treated specimens was tested according to EN 117 and the results are presented in Table 4-7.

The results of these termite experiments observed the same trends as the termite test results in Chapter 3 (Tannin-boron original formulation). The ε-caprolactam-containing formulation warranties lower weight loss and better visual rating compared to tannin-boron formulation. The only exception occurs for EN 84 leached samples that look still considerably degraded notwithstanding the extermination of the insect. Actually this formulation show improved protection properties but underline the necessity of a repellence agent in order to complete the effectiveness of the protection.

Table 4-7 Performance of the different wood preservatives against termites

Formulation	Leaching norm	Worker survival rate (%)	Weight loss (%)	Visual rate (%)				
				0	1	2	3	4
Control	-	71.82 (9.18)	10.22 (1.05)	0	0	0	0	100
Boric acid	Unleached	0	1.54 (2.16)	16.7	83.3	0	0	0
	ENV 1250-2	0	2.31 (1.72)	0	0	0	50.0	50.0
	EN 84	55.47 (7.95)	11.33 (3.45)	0	0	0	0	100
Tannin-boron*	Unleached	0	2.4 (0.4)	1				
	ENV 1250-2	0	1.5 (0.1)	2				
Tannin-boron-ε-Caprolactam	Unleached	0	1.45 (0.16)	50.0	50.0	0	0	0
	ENV1250-2	0	0.65 (0.31)	0	50.0	50.0	0	0
	EN 84	0	1.92 (0.23)	0	0	0	83.3	16.7

Note: * These tests were realized with formulation containing 20% of tannin and 1% of boric acid (Tondi et al. 2012b).

4.3.7 Fireproofing behaviors

The simplified lab-scale combustion unit consists of a Bunsen burner, a three-legged bracket and a piece of metal net sheet, which has performed a test of two-minute fire exposure. In fact, short-time exposure tests simulate the lighting of the fire, while the weight loss test allowed a clearer understanding of the behavior of the wood specimens in the case of prolonged fire.

In this study, these parameters of ignition, flame and ember time represent a good evaluation of the ignition process (Table 4-8).

This simplified apparatus presents the result easily being influenced by the individual operator. Therefore, experimental data could be different with other tests in previous works. However, the analysis of the table still shows the fire-resistance properties of treated samples with advanced tannin-based preservative excluding man-induce factors (done by the same person). The information achieved with this method allows only a preliminary notion of the general behavior of treated wood against fire.

The ignition time slightly increased when wood was introduced with the advanced tannin-based formulation. In the table 4-8, the flame time nearly is similar among the results of different sample systems. Only little or no effect can be observed for the ember time. The ANOVA analysis did not reveal any differences between values, whatever the treatment (P-value = 0.65).

Table 4-8 Short-exposure fire tests for Scots pine treated with tannin-boron-ε-caprolactam preservatives

Samples treatment	Ignition time (s)	Flame time (s)	Ember time (min)
Control	8.60	192.00	4.90
Only impregnation	12.75	185.00	3.88
EN113	13.33	179.00	4.03
ENV1250-2+ EN113	12.33	180.00	4.20
EN84+ EN113	13.00	178.33	4.22
EN117	13.33	178.33	3.83
ENV1250-2+ EN117	12.67	180.00	4.06
EN84+ EN117	12.67	178.33	4.03

4.3.8 Mechanical properties

Concerning the MOE and MOR, mean values did not indicate a trend following the boron concentration (Table 4-9). Furthermore, the bending test results of different boron-treated specimens did not express an agreed change with comparison to the untreated wood. However, MOE and MOR of wood treated with acid tannin-based solution advanced by ε-caprolactam, were likely superior to other partial formulations. Seemingly, MOR of beech wood treated with advanced tannin-boron preservative increased contrary to the controls.

Table 4-9 Statistical data characterizing mechanical behaviour of treated wood

Formulation		0%	1%	1.5%	2%	2%(No NaOH)	2.5%	3%	Control
Modulus of elasticity (MPa)	Beech	10242	11516	9782	10951	13592	12673	14158	12604
	Scots Pine	10239	11850	10783	12475	11361	12822	10431	11564
Modulus of rupture (MPa)	Beech	139.93	150.35	142.44	143.05	173.18	181.18	207.26	136.65
	Scots Pine	108.19	113.78	96.78	127.80	122.65	140.00	122.32	110.52

4.3.9. Laboratory biodegradation of soil in microcosms

The brown wood samples treated with tannin-caprolactam solution at a pH value of 9 were continuously leaching some tannin polymers during the field exposure, probably some borons. The figures 4-21 and 4-22 present the aspects of the samples after the unsterile soil-bed test. The colour of the test specimens turned lighter after the tests in Montpellier site (figure 4-21). Unlike the visual change of light-brown specimens, however, the superficial color layer of sample slowly altered and presented darker color at the moment of ending tests (figure 4-22). The discoloration observed on the weak-alkali tannin-treated samples was less important than

the discoloration on the samples impregnated with acid tannin solution, although the colour of all the samples turned grey.

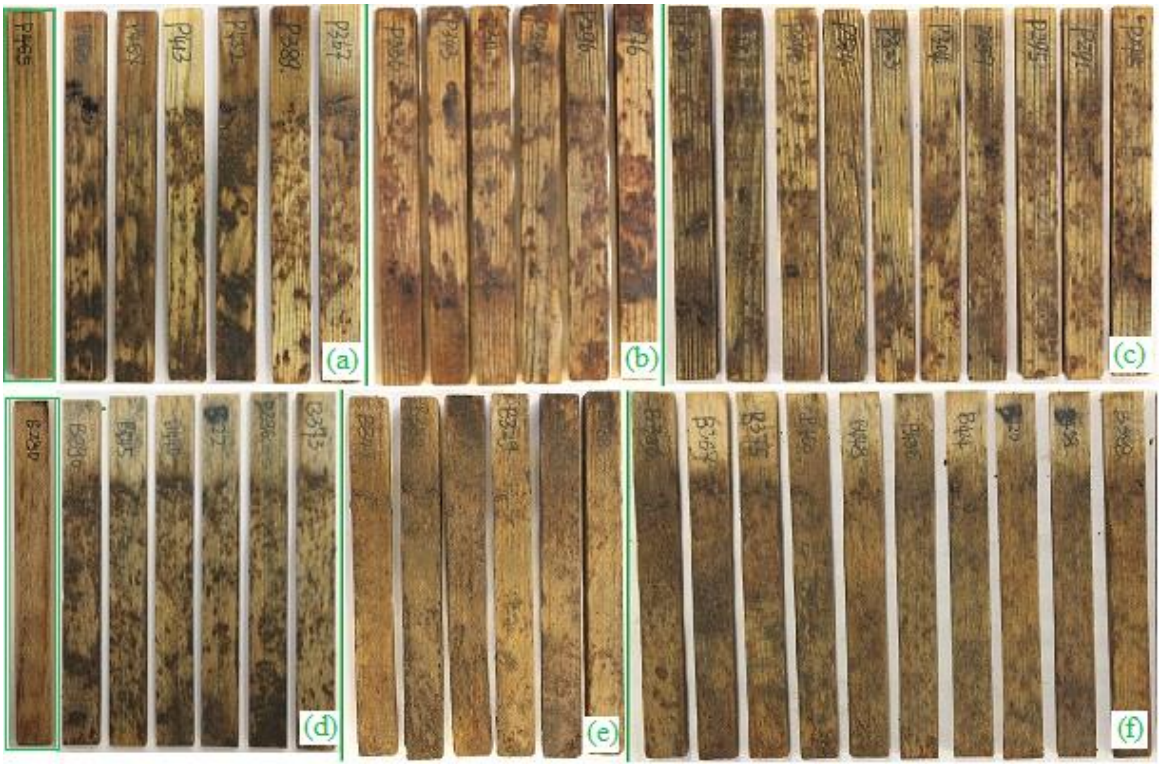


Figure 4-21 Visual pine and beech samples treated with tannin-caprolactam solution at pH=9 after the exposure in natural soil (Montpellier): a and d-3 months, b and e-6 months, c and f-12 months; "P"-pine wood, "B"-beech wood

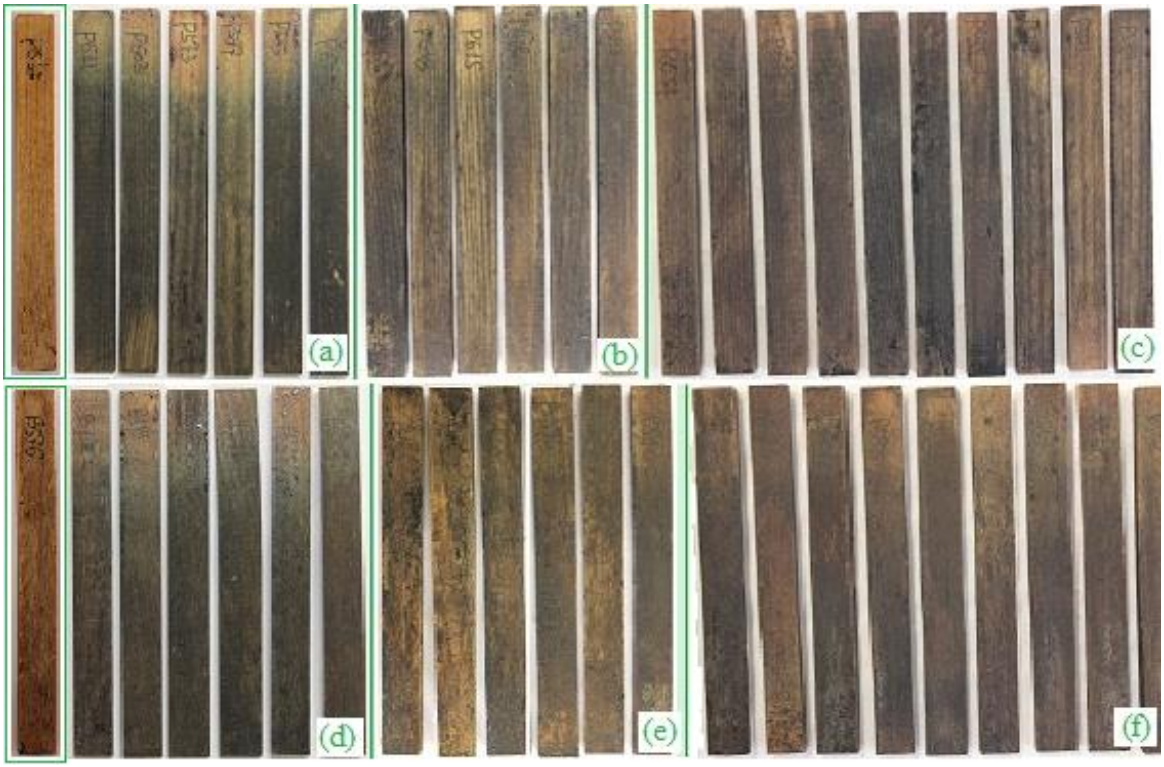


Figure 4-22 Visual pine and beech samples treated with tannin-caprolactam solution without adding NaOH at pH=4.5 after the exposure in natural soil (Changsha): a and d-3 months, b and e-6 months, c and f-12 months; "P"-pine wood, "B"-beech wood

The weight loss after several months' exposure in different soil of microcosms were arranged in figure 4-23 to 4-27, calculated as mean values of at least six specimens. The standard deviation of each group data was also indicated in the table (Annex F). Each time test specimens were removed , their moisture content was monitored between 45% and 80% excluding African padauk wood (15% moisture content of 3-month exposure, 33% moisture content of others) (data not shown). Microorganisms in Montpellier seemly attacked stronger than others in Changsha, because the mass losses of samples in Montpellier were more than the one observed in Changsha for the same exposure time. At the beginning of three months, the efficiencies of tannin-based formulations were not distinct, even the weight losses of some controls were less. It was emphasized that tannin treatment only cannot control fungi decay during the total experiment from start to end. All in all, the resistance of pine wood was better than the beech one, no matter how treated or untreated.

In the following figures, the controls compared with associated treated specimens come from the same test container. Figure 4-27, represents the results for the controls only (i.e. controls alone, with no other treated wood in a test container).

At the beginning of three months in the figure 4-23, the weight losses of all treated specimens were higher than that of controls. Until six months, the boron concentration of up to 2.5% and 2.0% without NaOH additives brought about a better effect of fungi resistance with comparison to controls. Between the results of 10 months and 12 months, the pine controls had a higher mass loss than the treated samples, except for the treatment with tannin alone. Regarding the mass loss results of three months as a baseline, the rates of subsequent mass loss for treated samples were lower than controls.

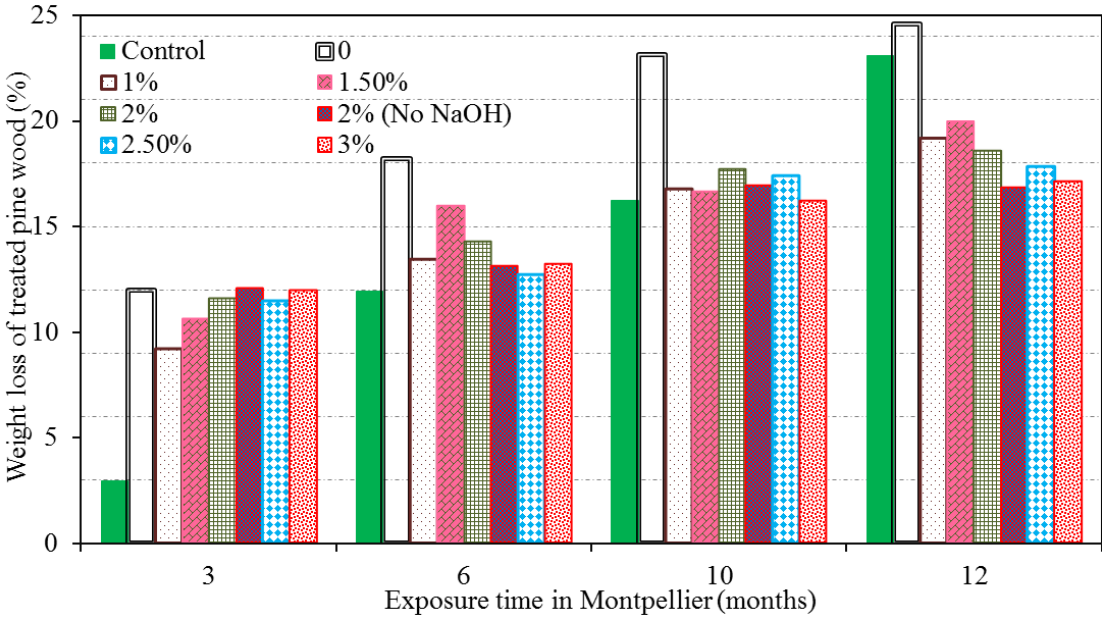


Figure 4-23 Weight losses in the pine specimens treated with tannin-boron-caprolactam preservative exposed to the microorganism in unsterilised soil from Montpellier (France) for 3, 6, 10 and 12 months

From the figure 4-24, it could be concluded: the controls always degraded much more than the treated samples when being performed the attack assays of microorganisms in unsterilised soil. For beech wood, the behavior of fungi resistance for treated pine was similar according to the rate of mass loss after three months. Furthermore, only tannin treated beech wood

showed worse performance than tannin and boron containing treatment against fungi in the unsterilised soil.

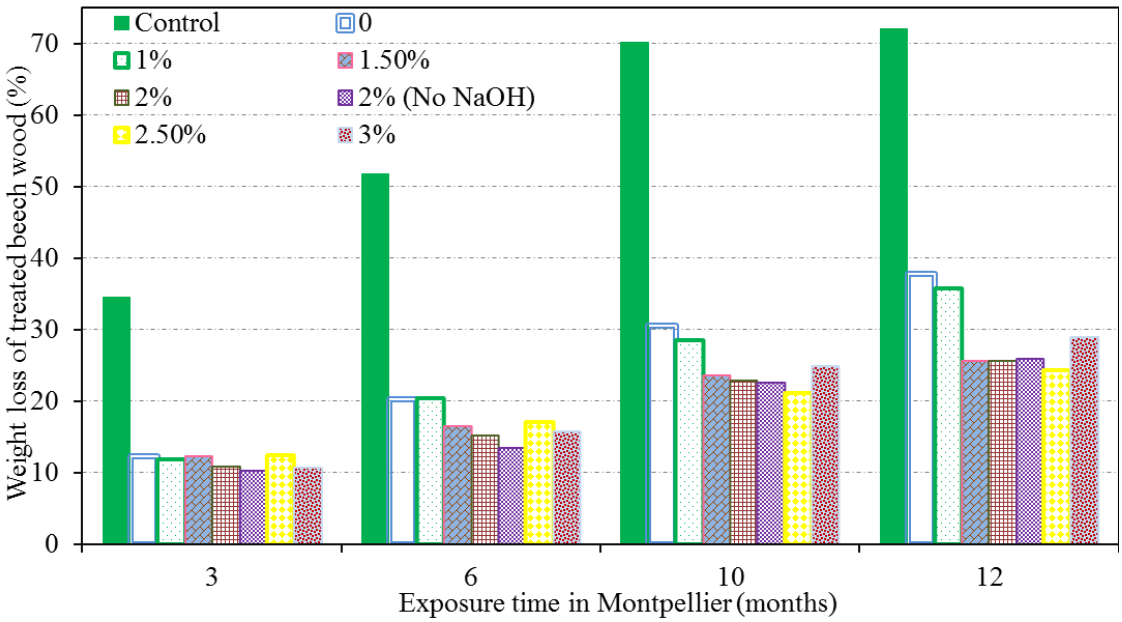


Figure 4-24 Weight losses in the beech specimens treated with tannin-boron-caprolactam preservative exposed to the microorganism in unsterilised soil from Montpellier (France) for 3, 6, 10 and 12 months

From the figure 4-25, the fungi resistance of treated pine samples (excluding tannin only treatment) was still relatively high after 12-month exposure in Changsha. Especially compared with the previous results of 6 and 10-month exposure, the lower weight losses of some treated formulations were presented. It was notable that the acid-impregnated solution (without NaOH) led to a significant mass loss of treated wood in 3-month exposure.

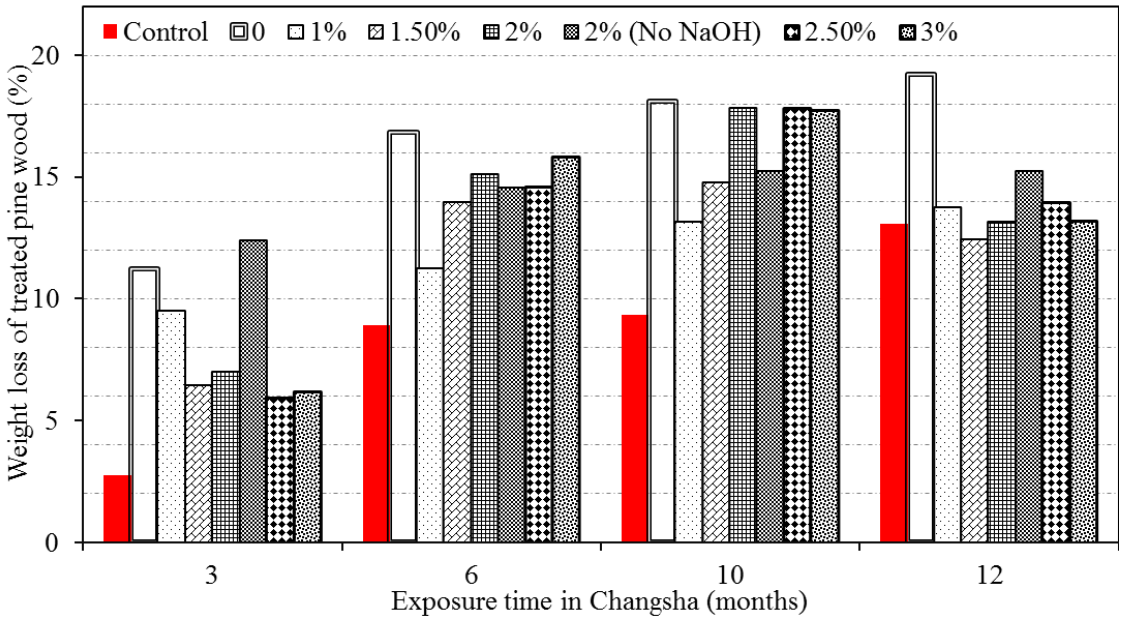


Figure 4-25 Weight losses in the pine specimens treated with tannin-boron-caprolactam preservative exposed to the microorganism in unsterilised soil from Changsha (China) for 3, 6, 10 and 12 months

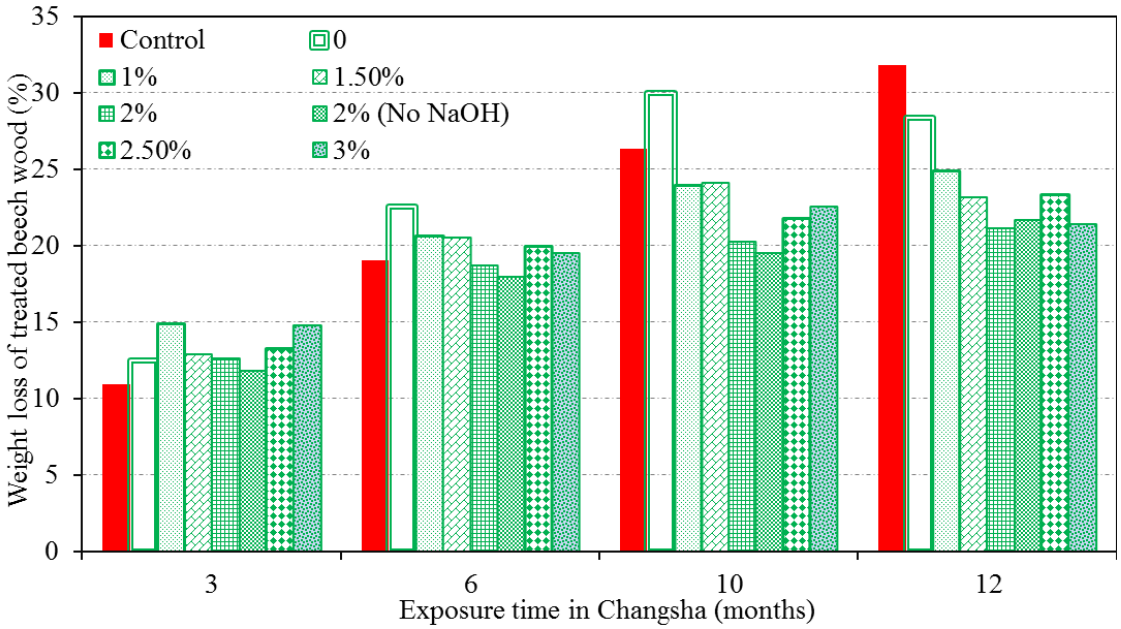


Figure 4-26 Weight losses in the beech specimens treated with tannin-boron-caprolactam preservative exposed to the microorganism in unsterilised soil from Changsha (China) for 3, 6, 10 and 12 months

The figure 4-26 presented the mass losses of treated beech samples. These formulations after 3-month exposure in Changsha indicated a little different effect. The fungi resistance of treated wood specimen with tannin only always presented a worse performance, exception done for three months exposure.

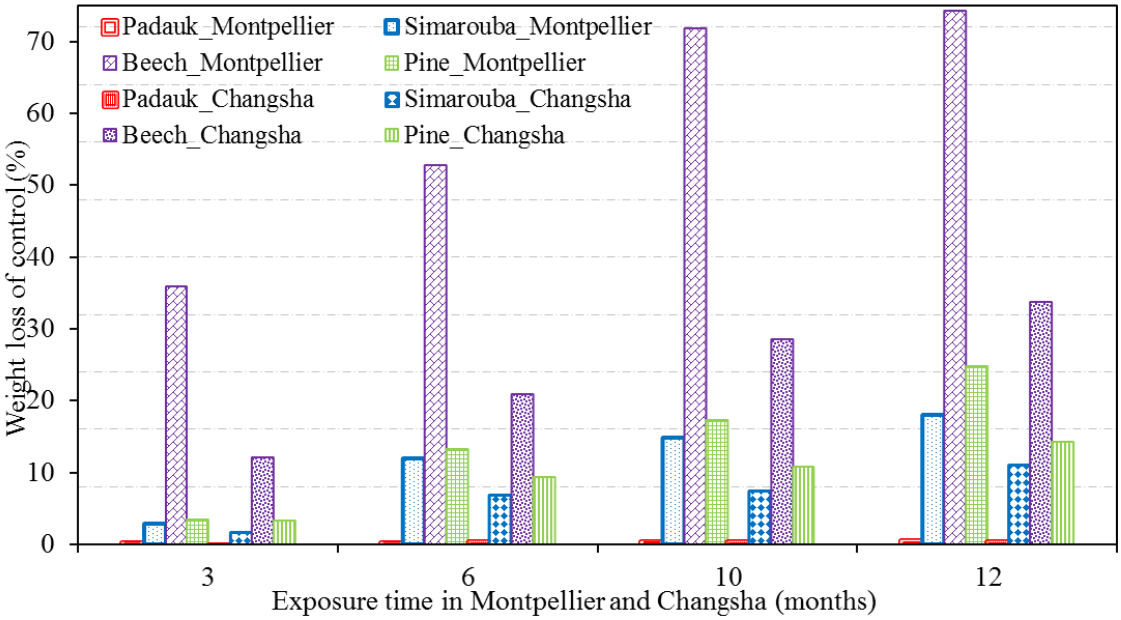


Figure 4-27 Weight losses in four control specimens exposed to the microorganism in unsterilised soil from Montpellier (France) and Changsha (China) for 3, 6, 10 and 12 months

The figure 4-27 analysed the soil microorganism resistance of all control samples from 3 months to 12 months in Montpellier and Changsha. African padauk with a weight loss of less than 0.5 was classified and ranked the natural fungal durability of very resistance, as already stated Nzokou et al (2005). Simarouba resisted fungi attacks was limited, but its effect was

better than beech wood and pine sapwood. Beech wood was subject to severely degrade, which belonged to very susceptible timber to wood decay. The weight loss of pine wood was less than 20%, even in Montpellier.

Figure 4-28 presented the visual shape of exposed samples which were dried to anhydrous status. Padauk wood kept its straight strip when subjected to 103 ℃. However, the very big bow of soil-immersed end in beech wood was appeared when it was stayed in the oven; and then it was inferred that in the soil rots were very active.

Figure 4-28 The visual morphology of anhydrous samples after the exposure in soils

4.4 Discussions

As described by Pizzi and Baecker (1996), the reaction of tannin and boric acid was based on the Lewis acid acceptance of electrons from the ether oxygen of the flavonoid unit pyran ring with concurrent and consequent facilitation of base induced heterocycle opening. In a word, the reaction of autocondensation of flavonoid tannins induced by weak Lewis acids, included boric acid, proceeds at an elevated rate. FTIR spectra progressively proved that boric acid catalysis didn't involve the reaction of orthodiphenol complexation with the B-ring of flavonoids which was already well-known. In fact, the complexation of the boric acid with the model compound of the B-ring of tannin was the favourite reaction, followed by the complexation with the model of guaiacyl units of lignin, and last by the model of the carbohydroxides from either the tannin or the substrate. The reactive site so formed was blocked, by the charge of the Lewis acid counterion, from undergoing the intramolecular bond rotations generally associated with intramolecular rearrangements of the unit. Therefore, the effect addressed the subsequent condensation of the reactive site formed away from internal rearrangements and towards condensation with a flavonoid unit in another polymer chain.

Only tannin autocondensation forming the resin, it didn't obey the demand of boron-anchored preservative because of its solubility. When used as a hardener for tannin adhesives it gave gel times faster than formaldehyde, hexamine was interesting that with tannins and other adhesives it yielded wood products of very low formaldehyde emission. Those studies of tannin resin had shown to react and cross-link with hexamine by the formation of rather stable benzylamine or hexamine derived aminomethylene bridges (Pizzi and Tekely 1995, Pizzi et al. 1994), furthermore, some information proved this resin could be applied in exterior grade products (Pizzi et al. 1994, Pizzi et al. 1997). Once the crosslinking network between tannin and hexamine formed, the resin was insoluble (Pena et al. 2009). From the analysis performed by FTIR in this study, it can be concluded that ether and amine groups were the ones obtained

from curing reactions between tannin and hexamine as Pichelin et al. (1999) and Pizzi and Tekely (1995) had proved by NMR analysis.

In this work, ε-caprolactam was mixed in the tannin-hexamine resin because of improving its rigidity. FTIR spectra were analysed to illustrate caprolactam in the branch of tannin polymer. On the other hand, it could not be shown that ε-caprolactam reacted with boric acid. ^{13}C-NMR was introduced to progressively explain the mechanisms among tannin, hexamine and ε-caprolactam. Unfortunately, obtained resin could dissolve in some solvents. On the contrary, it proved that tannin-caprolactam-hexamine resin was produced by crosslinking reaction and certainly not soluble.

It was clearly shown that ε-caprolactam does not disturb the reaction previously studied between tannin, boric acid and hexamine. The tannin-boric acid-hexamine association can still create a waterproof polymer network in the presence of ε-caprolactam.

The color of tannin preservative-treated timbers was brown, because the visual sense of tannin-based solution ruled it. However, the color could alter after the deteriorated process, even in this advanced tannin-based preservative. The soil exposure provided comparable results in terms of visual changes in superficial colour of samples.

The tannin solution of lower pH value had a higher viscosity. Therefore, the impregnation of the tannins solutions is more superficial than for the other samples.

So there were few tannin polymer networks in the inner parts of treated wood because of the foregoing formed obstacle. Once the superficial layer of treated was totally broken, the nearly virgin wood was subjected to biological attacks. Another point of view, a good compromise between low viscosity and high reactivity of tannin solution should be followed, as Tondi et al. (2013b) had proved by some analyzed means.

Therefore, the analyses of tannin-based preservatives' retention were very important. It could explain some phenomena of solution/liquid fixing in wood resulted in some variations of wood properties (i.e. color). On the other hand, the retention could indicate the efficiency/threshold of the active ingredients. For example, in this study the biologically active component in these wood preservatives was boron. In our formulations, tannins alone did not provide any protection to wood as shown by Thevenon et al (2009), and as previously stated by (Laks and Kaig 1988, Dirol and Scalbert 1991).

The wood preservative uptake was possibly the most important parameter to be investigated when a wood preservative was tested. It was observed that the scots pine samples were generally easily impregnable with low tannin content formulations.

The retention of tannin/boric acid/ PEG presented a relatively high value, because the PEG is high-molecular-weight. In reality, the samples treated with PEG had a high standard deviation because the surface presented an observable layer of viscous skin which became much thicker as soon as the samples were kept under water for a while. This PEG glutinous skin was probably due to the accumulation of un-penetrated PEG and therefore also the analyses of the results have to consider this behaviour (Tondi et al, 2015).

The presence of caprolactam and PEG additives allowed a higher total retention of the 10% tannin formulation and simultaneously enhanced the amount of solid preservative in the structure. Actually, with comparison to boron retention in wood treated with tannin-boron-caprolactam formulation, the liquid uptake of boric acid was little lower for the samples

treated with 10% tannin solution of PEG additives. This was possibly result in by the barrier effect of PEG.

It can be seen that the new formulations had a lower tannin and boron content than the original tannin-boron formulation (Thevenon et al. 2009), but the biological performances of this advanced formulation are enhanced

Every water-borne formulation used in wood protection science was sensitive to the leaching action of the water. Hence, the tannin-hexamine networks were also affected by this phenomenon and the quantification of its leachability was fundamental for the industrialization process of these formulations. In the figure 4-20, the leachate analyses (ENV 1250-2) presented a desirable effect for tannin/boron/caprolactam. This leaching protocol was regarded being a moderate test among all the existing tests of leaching.

Even if the results of leaching were very encouraging, the study of the biocidal capacity of the advanced tannin-boron formulations was not obvious. ε-caprolactam contains a nitrogen atom. Indeed, in many occasion occurs that nitrogen-containing molecules result more easily attacked by biological degradation agents (Ouchiyama et al. 1993). For this reason, and to evaluate the boron fixation, complete overview of biological test was performed by in the laboratories. Successively, the comparative leaching tests proved that advanced tannin-hexamine formulation can fix boron better than other tannin-based formulation. Moreover, biosusceptibility to fungi had been proposed that wood block treated with advanced tannin-based preservatives can ideally prevent these biological factors. Even if the current amount of boron was lower, the advanced tannin-based formulations containing ε-caprolactam showed the much higher resistance to *Antrodia spp.* attacks even after the very aggressive leaching (EN 84) and *Coniophora puteana* decay including subject to leaching (ENV 1250-2). The decay of samples with tannin/boron/caprolactam formulation to termite attacks also showed positive potential in table 4-7. In the case of termites, as boron is not repellent, even if the attack is drastically reduced, the insects still have to ingest some treated wood before dying. Caprolactam played an important role in progressively limiting boron leachability. Lower boron losses in tannin/boron/caprolactam-treated wood specimens showed resistance to decay by fungi and termites. It was possible to conclude that chemical modification of tannin/boron-treated wood by strengthening the branch of tannin polymers with ε-caprolactam can improve the properties of wood, resulting in more biological resistance to wood degrading organisms (Goldblatt et al. 1954, GWQS 2002).

It was interesting that unsterile soil-bed tests likely proved the effect of advanced tannin-based preservative with ε-caprolactam. The biological deterioration with the laboratory Basidiomycete tests (EN113) does not reflect the complete reality, as wood in service can be subjected to very diverse fungal attacks. Generally, the wood-destroying microorganisms in soil are brown rot, soft rot and white rot, and depending on the conditions (soil, pH, temperature, humidity…), they can be active differently. In Changsha, there was no laboratory which can be set the constant temperature and humidity. The decay resistances in natural climate were different than ones in Montpellier.

During the initial three months, weight losses of treated wood were possibly due to leaching of tannin reacted or unreacted products. Thus, the results of the soil tests have been expressed with the weight loss after 3 months exposure as a new baseline (Fig 4-29, 4-30, 4-31).

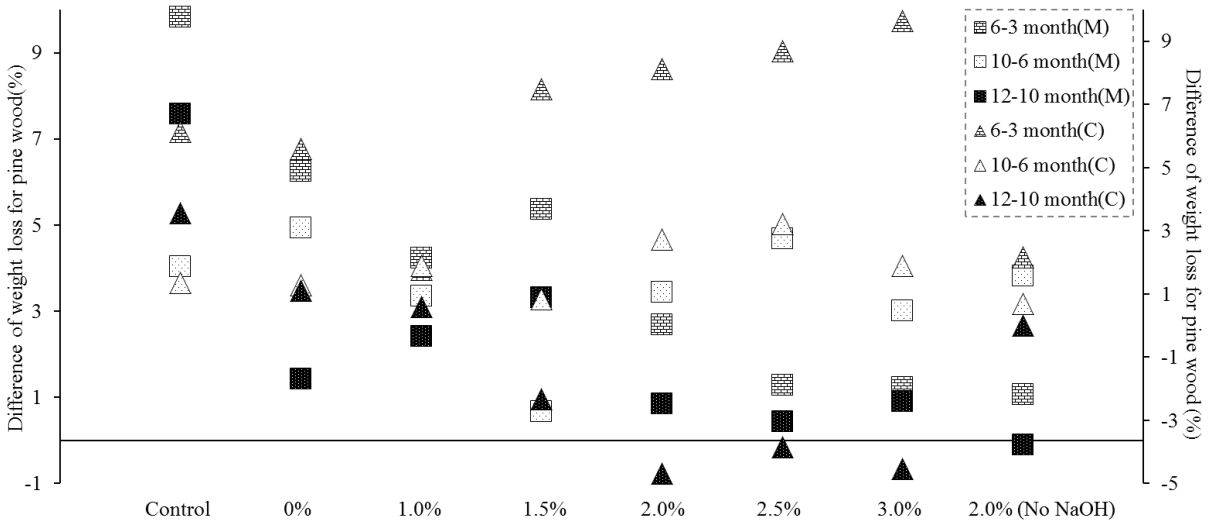


Figure 4-29 The interactive difference of weight losses in the pine specimens treated with tannin-boron-caprolactam preservative exposed to the microorganism in unsterilised soil from Montpellier (France) and Changsha (China)

From the figure 4-29, when considering, the mass loss of treated wood in Montpellier diffused between 0.9% and 6.42% to pine wood, as well as 1.92% and 10.2% to beech wood. Likewise, the treated wood decay in Changsha based at the results of three months presented a similar rule. Furthermore, the results of some treated samples (i.e. 1.5%, 2%, 2.5% and 3% boron treated pine wood; as well as 0%, 1.5% and 2.5% boron treated beech wood) after twelve months were not considered significantly discriminant (Figure 4-30).

The evaluation of the decay had proved that weight loss of controls were higher when they were not in presence of treated wood samples (i.e. controls only in a test container). This is the reason why boric acid alone was not considered as a treatment for this set of experiment. Indeed, naturally some soils can be more biologically active than others, and the boron leaching from each treated sample could affect the activity of the soil fungi.

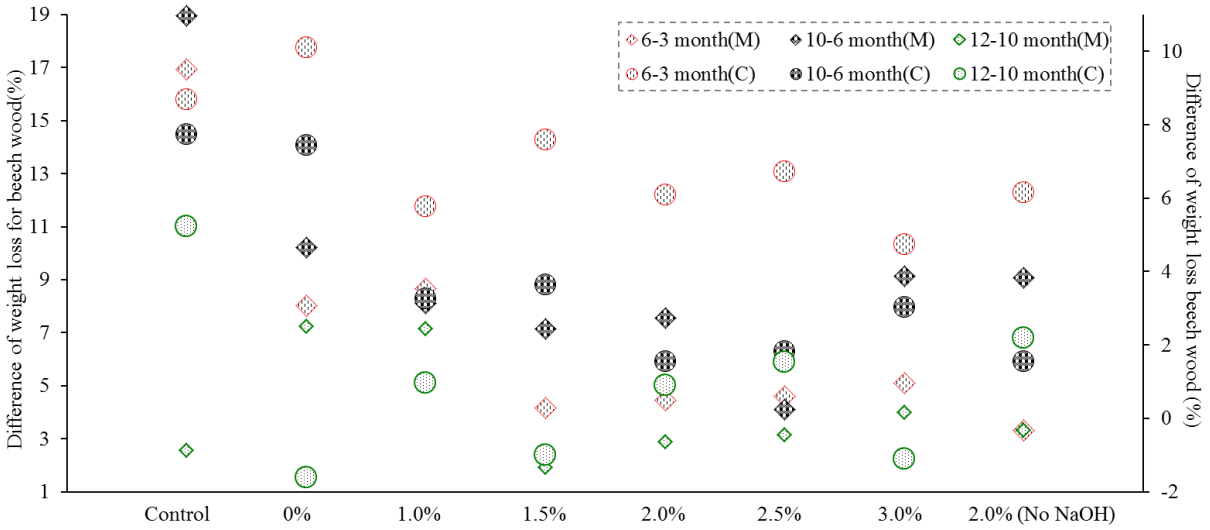


Figure 4-30 The interactive difference of weight losses in the beech specimens treated with tannin-boron-caprolactam preservative exposed to the microorganism in unsterilised soil from Montpellier (France) and Changsha (China)

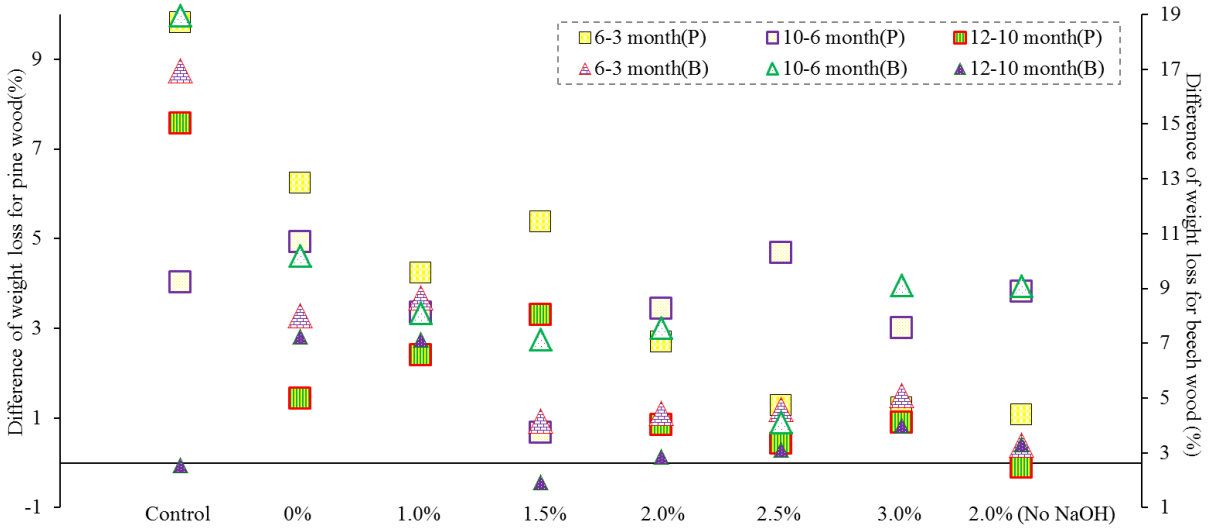


Figure 4-31 The interactive difference of weight losses in the beech and pine specimens untreated/treated with tannin-boron-caprolactam preservative exposed to the microorganism in unsterilised soil from Montpellier (France)

From the figure 4-31 (result in Montpellier), during the beginning of six months the treated pine and beech wood including 1% boric acid were decreased about 6.24% and 8.01% of their weight, respectively. Nevertheless, the weight loss of control pine and beech separately achieved 13.22% and 52.80%. With the development of exposure time, the weight of control quickly fell, compared the treated wood. At the end of assay, the maximum weight losses of treated soft and hard wood in these formulations were separately 10.01% (1% boric acid) and 23.90% (1% boric acid). However, pine and beech controls had respectively reduced 24.83% and 74.32% when they were moved out from the soil for 12 months.

The results also presented that beech was more degraded than pine, which indicating that fibrous rots were predominant in both types of soil. Then the lighter colour of the tannin treated samples can be the resultant of a combination of tannin leaching and with rot activity.

Nevertheless, considering the moderate weight loss of pine, as well as deformation after drying at 103 ℃, even if not predominant, cubic and/or soft rots were active in the soils (appearance of deteriorated wood sample in the oven also could prove loss of fibers in wood samples). But this did not mean that there was no action or interaction of cubic of soft rots. In fact, wood can be ruined by three main wood-destroying fungi: brown rot (so-called “cubic rot”), white rot (so-called “fibrous rot”) and soft rot. Brown rot fungi mainly degraded the wood’s carbohydrates, i.e. the cellulose and hemicelluloses, which were mainly found in coniferous wood. White rot fungi degraded both the lignin and the cellulose in the wood cell walls, by which hardwood was more readily attacked than softwood. Soft rot fungi degraded the carbohydrates in the wood cell wall, which can attack all coniferous and hardwoods (Eriksson et al. 1990).

To the timber treated with boron-based preservatives, an effective fungicidal performance had been proved (Cockcroft and Levy 1973, Lloyd 1998, Obanda et al. 2008). Boron threshold was around 0.5% for *Basidiomycetes* (fibrous and cubic rots); but boron was not very effective against soft rot (Freeman et al. 2009). The toxic threshold from the soil contact tests on pine and beech indicated a boric acid retention of <1.6 kg/m^3 and 1.6 kg/m^3 respectively, which could prevent the onset of cubic rot and fibrous rot (Drysdale 1994, Annex G).

Concerning the toxic threshold of boric acid, white rot was seemly a bit higher than brown rots. Therefore, in these unsterile soil tests all formulations could nearly protect the wood samples treated with tannin-based preservative modified by caprolactam. Especially, the highest concentration of boric acid up to 3% had prevented a large number of wood decay (fig 4-31).

Considering fire proofing, it was worth noting that tannin/boron/caprolactam-treated and biologically deteriorated specimens suffered short-term exposure but were not identified a significantly different result with impregnation only. Furthermore, with comparison to control the fireproofing properties still were improved. However, this result was worse than the effect published by Tondi et al (2012). Firstly, this retardant effect should owe to inorganic boron and tannin-hexamine copolymers. Secondly, the effect of caprolactam probably appeared to weaken the fire retardancy of this system, because caprolactam was the textile materials being sensitive to fire (Van Rijswijk et al. 2009).

4.5 Conclusions

(1) The structure of tannin polymer did not change with additive of ε-caprolactam, but it was assumed that ε-caprolactam had successfully been connected on the branch of tannin polymer.

(2) The presence of ε-caprolactam did not really modify the retention of tannin and boric acid.

(3) The colour of samples treated with tannin/boron/caprolactam still appeared brown.

(4) The polymerization of tannin and hexamine included actively the ε-caprolactam in the network and the boron fixation results even enhanced.

(5) ε-Caprolactam modified the rigidity of the tannin polymer; furthermore the advanced formulation underlined the fungi resistance.

(6) Fire retardancy of specimens treated with tannin/boron/caprolactam formulation could be kept, but the efficiency decreased.

(7) MOR and MOE of treated with tannin/boron/caprolactam preservative were not obviously altered.

(8) From these results, it appears that tannin-boron-caprolactam formulations, once impregnated and reacted into the wood can provide a sufficient protection for a use class 3 (even use class 3.2 above ground, un-protected exposure). The unsterile soil-bed tests have also shown that these formulations do provide protection in a very difficult biological hazard situation. The results of the MOE and MOR after the different field test exposure time should provide interesting answers about the remaining strength of the samples (experiment to be performed).

Moreover, they have proved to be efficient against termites attack (even if the visual rating criteria imposed by the standard are not as much in favor as the weight loss of the samples). A choice test should be performed to check the termite behavior in a real scenario.

5. Wood polymer nanocomposite based tannin resin and montmorillonite

5.1 Introduction

Now-a-days, nanotechnology covers a wide range of area in science and technology. Since many important physical and chemical interactions are governed by surface and surface properties, a nano structured material could have substantially different properties from a conventional composite of same composition. Likewise, wood polymer nanocomposites can provide a new way to overcome the limitations of traditional counterparts, such as high moisture uptake, dimensional variation, biodegradability, high strength, flammability, thermal stability, and so on.

However, the miscibility between inorganics and organic wood was one of the key problems to allow making wood nanocomposite.

Therefore, using a polymer as a carrier was very important, in order to introduce introduced inorganic nanoparticles in wood. Once significantly increased interfacial interaction between inorganic and organic phases and size-dependent phenomena of nanoscale particles, wood polymer nanocomposites were capable of dramatically improving several properties. A number of wood nanocomposites based on wood flour/polymer/inorganics (i.e. montmorillonite) have been reported (Zhao et al. 2006, Lee et al. 2008, Deka et al. 2011). However, a few studies that inorganic particles were impregnated into solid wood were published, for example, wood polymer nanocomposite by using water-soluble PF resin and montmorillonite (Xue and Zhao 2008), solid aspen wood with MUF resin in combination with hydrophilic and hydrophobic montmorillonite (Cai et al. 2008). Actually, fabrication of wood polymer nanocomposites was one of the promising techniques used to improve the properties of wood by impregnating a polymer.

In this study, a plant-based tannin resin was prepared followed by dispersion of montmorillonite (MMT) into it. Wood tannin-polymer nanocomposites (WTNC) were performed by impregnating an MMT-dispersed tannin polymer (containing boric acid) into wood in the presence of a hexamine as a hardener. This work aimed at inspecting the various properties of WTNC.

5.2 Materials and methods

5.2.1 Wood and reagent

Various sizes of wood samples of Scots pine sapwood (*Pinus sylvestris*) and beech (*Fagus sylvatica*) were prepared and placed in a climate chamber (20 ℃ and 65% RH) up to constant weight, prior to treatment.

Unless otherwise stated, chemicals were from Sigma-Aldrich and were of analytical grade. The used Na-montmorillonite (MMT) with purity of 95-98% was purchased from Zhejiang Fenghong Clay Chemicals Co., Ltd (China). Cetyl trimethylammonium bromide (CTAB) was

from Jiangsu Chemical Plant (China). For all assays, deionized water (grade 3, ISO 3696) was used. Mimosa (*Acacia mearnsii*) tannin extract was prepared by Silva Chimica (Italy).

5.2.2 Preparation of organomodified MMT (OMMT)

Fifty grams of MMT were dissolved into 1 liter of water. After stirring for 1.5 h, CTAB was dispersed into the solution by a ratio 135 mmol/100 g with MMT. The reaction mixture was intensively stirred for 2 h at 80 ℃. Then it was left to stand at room temperature for 24 h, and after decantation, the solution was replaced with the deionized water. The former white precipitate was isolated by filtration, and the excess of bromide and organic ions in the organoclay was removed by repeated washing with the deionized water until a negative result of the 1% $AgNO_3$ test was obtained (no light yellow deposit) (Tsunashima et al. 1981). OMMT was dried in air first at room temperature and then at 60 ℃. The final product obtained was ground with a mortar and a pestle, and the <200 mesh-size (<74 μm) fraction was collected.

5.2.3 Preparation of wood tannin-polymer nanocomposites (WTNC)

The tannin-hexamine-boron solutions were done the same way as described in Chapter 3. Once the pH was adjusted to 9 (with a 50%NaOH solution), the OMMT was added to the solution and stirred. The concentration of each ingredient was presented in table 5-1. All of the samples were oven-dried at 103 ℃ to constant weight before treatment and weighed (M_0). The impregnation protocol is described in Chapter 4.

After impregnation, the samples were cured at 103 ℃ for 12 hours.

Table 5-1 Proportions of components in the solution of tannin-boron resin and OMMT

Additive / Formulation	Tannin (%)	Boric Acid (%)	Hexamine (%)	NaOH (%)	OMMT (%)	Water (%)
Free Boric Acid and OMMT	-	0.41	-	-	3.00	96.59
Tannin-Boron-OMMT (with Hexamine)	7.55	0.41	0.49	0.49	3.00	88.55
Tannin-Boron-OMMT (without hexamine)	7.55	0.41	-	0.44	3.00	88.60

The retention of the products was calculated referring to equation (4-1) of "4.2.5 Impregnation scheme" in Chapter 4.

5.2.4 Fourier transform-infrared spectroscopy (FT-IR) analyses

In this study, FT-IR was performed on the described samples as follow, which were ground prior to FT-IR analysis:

(1) Polymer alone - A small quantity of treatment solution (table 5-1) excluding the free boric acid and OMMT was heated at 103 ℃ until complete polymerization/solidification.

(2) Pine sapwood or beech impregnated with the treatment solutions - A thin slice from tangential and radial faces was taken from the treated and cured wood samples.

The FT-IR protocol was referred to §4.2.3 in Chapter 4.

5.2.5 X-ray diffraction (XRD) analysis

The degree of nanoclay dispersion and OMMT distribution in the WTNC were evaluated by XRD analysis. X-ray diffraction was performed on powder of polymer alone and treated wood obtained in the same way as for FTIR analyses. It was carried out on an X-ray diffractometer (Bruker D5000, Bruker AXS GmbH, Karlsruhe, Germany). All composite samples were analyzed on transmission mode. The X-ray beam was Cu Kα (λ=0.154 nm) radiation operated at 30 kV and 100 mA. The powder samples were mounted on a sample holder with a large cavity and a smooth surface was obtained by pressing the powders with a glass plate. The scanning rate was 1°/min and 2θ ranged from 1.5° to 40° with the rotation speed of 30 rpm. The basal spacing of the silicate layered, were determined from the Bragg's equation:

$$d=\frac{n\lambda}{2\sin\theta} \quad (5\text{-}1)$$

where d is the interplanar distance (nm), θ is the diffraction position and λ is the wavelength (nm).

5.2.6 Transmission light microscopy (TLM) observations

Small samples of dimensions 10×5×5 mm^3 (L, R, T) were taken from the outer part of a larger sample (50×25×15 mm^3, L, R, T) impregnated with complexes of tannin-hexamine- boron resin and OMMT. For normal light microscopy, wood samples were embedded in paraplast using standard resin embedding techniques. The wood segments were dehydrated through a gradient of ethanol and infiltrated with LR White resin using solutions of 25:75, 50:50, 75:25 (v/v) LR White resin/methanol for at least 5 h each and finally with 3 changes of 100% LR White resin for 5 h each. Samples were placed in polypropylene capsules, filled with fresh LR White resin and polymerized at 65 ℃ overnight. Once the samples were cured, it removed the gelatin capsule and cut the top of the sample to make it flat, using a razor knife. The sample was placed in the rotary microtome clamps, when it had been polished the cut surface with fine grain. One μm sections of LR White resin-embedded material were cut with a microtome equipped a diamond blade. Ultramicrocuts heat-fixed to glass slides were observed on a light photomicroscope (Leica microsystems) under phase contrast, bright field and dark field. Image capture was performed by means of a digital camera (1316×1034 pixels in 256 grey levels).

5.2.7 Scanning electron microscopy (SEM) observations

Small samples of dimensions 5×5×5 mm (L, R, T) were taken from the outer part of a larger sample (50×25×15 mm, L, R, T) treated with the complexes of tannin-hexamine-boron resin and OMMT. The wood block was then mounted on a standard SEM microscope stub, and sequentially coated with a layer of 60:40 platinum/palladium (thickness of ~20 nm) using a sputter coater. The block was placed inside a scanning electron microscopy (SEM, Quanta 450, FEI, Hillsboro, USA). An observation accelerating voltage of 15 and 20 KV was used to collect SEM photomicrographs.

5.2.8 Compression tests

The treated and untreated specimens for compression tests parallel to grain (60×20×20 mm^3;

L, R, T) were investigated according to the standard DIN 52185 (1976). Six pine and beech samples for each treatment formulation were tested in longitudinal direction (figure 5-1) using a constant displacement rate of 3 mm/min. The compression strength was performed on a universal testing machine (Zwick Z250, Zwick-Roell, Ulm, Germany).

Figure 5-1 Compression test

5.2.9 Surface properties

5.2.9.1 Hardness

The hardness was measured according to the Brinell test EN 1534 (2000). Six specimens (60×20×20 mm^3; L, R, T) for each treatment of each wood species were employed to determine hardness on their tangential and radial faces.

Using the EMCO Test Automat M4U 075 (Figure 5-2), a steel ball with 10 mm diameter was pressed with a defined force of 500 N into the sample and remained there for 30 s. The Brinell hardness was calculated applying the press force, the diameter of the steel ball and the diameter of the impression. An electronic calliper was used for the diameter measurements. Diameters were measured both parallel and perpendicular to the grain in order to take into account the anisotropy of wood.

Figure 5-2 Hardness test

The mean value of the two diameter measurements was used in calculating the result:

$$H_B = \frac{2 \times F}{\pi \times D\left(D - \sqrt{D^2 - d^2}\right)} \quad (5\text{-}2)$$

where H_B is the Brinell hardness in MPa, $\pi \approx 3.14$, F is the nominal force in newtons, D is the diameter of the steel ball in millimeters (10 mm), and d is the mean diameter of the residual indentation in millimeters.

5.2.9.2 Gluing tests

The gluing capacities of the treated surface with complexes of tannin-hexamine-boron resin and OMMT were assessed by means of a shearing test (figure 5-3) (Tondi et al. 2012a). Samples (of pine and beech 80×20×5 mm^3; L, R, T) were glued in couples with 250 g/m^2 of polyvinyl acetate (PVAc) based resin (D3 class, resistant to water). At least five glued samples for each formulation were obtained and tested. The shearing test was performed at a rate of 2 mm/min on a 20×10 mm^2 glued surface.

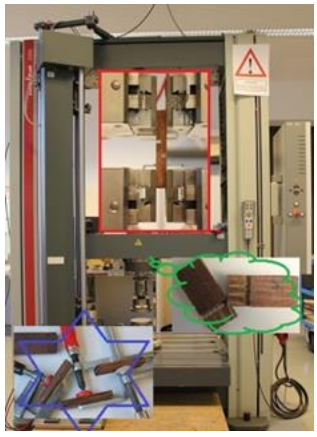


Figure 5-3 Gluing test

5.2.9.3 Contact angle measurements

Untouched exterior surface of the samples (of pine and beech) used for the gluing test (80×20×5 mm^3; L, R, T) were performed for the contact angle measurement. A high-resolution drop shape analysis system (DSA 10-MK2, KRUESS, Germany) was used to determine contact angle of wood samples. A drop of

deionized water from a syringe was placed on the specimen surface at room temperature. After the tip of the needle was separated from the drop, the charge-coupled device (CCD) camera captured the side view of water drop and the contact angle was measured in the recorded image by using drop shape analysis software, Scientific Drop Shape Analysis Software, DSA 1, Version 1.70 (KRUESS GmbH, Germany) and a curve fitting method (Tangent Method-1). Contact angle was measured for at least three specimens per treatment or control, and three locations per specimen.

5.2.10 Behaviour towards water

For Water Absorption (WA) and Dimension Swelling (DS) tests, wafers measuring of Scots pine and beech 10×20×20 mm^3 (L, R, T) were dried in an oven (103 ℃) before testing. Ten treated/untreated samples with complexes of tannin-hexamine resin and OMMT were submerged into beakers filled with water. The water was replaced with fresh one after 10, 20, 30, 40, 50, 60, 90 min and 2, 3, 4, 30, and 48 h. Meanwhile, the exchanged water was collected to use for analysing boron and tannin loss. Weights and dimensions of the samples were recorded. Experiments were carried out at 20 ℃.

5.2.10.1 Water absorption and dimension swelling test

WA (%) and DS (%) were calculated according to equations (5-3) and (5-4) after each water replacement:

$$\mathrm{WA} = \frac{W_t - W_0}{W_0} \times 100 \quad (5\text{-}3)$$

$$\mathrm{DS} = \frac{DS_t - DS_0}{DS_0} \times 100 \quad (5\text{-}4)$$

where W_t is the weight (g) after immersion in water for a specified time period, and W_0 is the oven dry weight (g); DS_t is the radial or tangential dimension (mm) at any given time during water soaked condition, DS_0 is the oven dry dimension (mm).

5.2.10.2 Water repellent effectiveness

Water Repellent Effectiveness (WRE) was measured for different soaking periods. Resistance to water uptake is expressed as WRE (%) and calculated as:

$$\mathrm{WRE} = \frac{WA_t - WA_0}{WA_0} \times 100 \quad (5\text{-}5)$$

where WA_t is the water uptake (equation 5-3, %) of treated wood samples immersed for 10, 20, 30, 40, 50, 60, 90 min and 2, 3, 4, 30, and 48 h. WA_0 is the water uptake (%) of untreated samples immersed for the same periods.

5.2.11 Dimensional stability test in vapor

Ten specimens of treated (only considering complexes of tannin-hexamine-boron resin and OMMT)/untreated pine and beech (10×20×20 mm^3; L, R, T), were selected to undergo dimensional stability tests. Wood blocks were monitored to evaluate their behaviour under various moisture conditions. The swollen and shrunken three dimensions and the weight of the samples were registered for 1 week by exposure to 0%, 10%, 20%, 30%, 50%, 60%, 80% and 90% relative humidity at 20 ℃. The dimensional swelling was referred according to the equation (5-4). The dimensional shrinkage was expressed as (Equation 5-6):

$$\text{Shrinkage Percentage (SH,\%)} = \frac{DS_1 - DS_0}{DS_0} \times 100 \quad (5\text{-}6)$$

where DS_1 is the radial or tangential dimension (mm) per shrunken stage, and DS_0 is the radial or tangential dimension (mm) under oven-dry condition.

5.2.12 Biological resistance test

5.2.12.1 Leaching performance

Prior to biological tests, half of the treated samples were leached.

Leaching was conducted to highlight the performance of retained boron and MMT in WTNC. The leaching procedures were performed according to the described program in "4.2.7 Leaching procedure". The leachates were kept at 4 ℃ for further analyses.

5.2.12.2 Biological tests

Due to the length of standardized fungal and termite tests (16 and 8 weeks of exposure respectively), screening tests were chosen to evaluate the biological performances of these treatments.

The decay tests were done according to the method described by Bravery (1978) for the fungal tests, and to an internal CIRAD protocol for the termite tests..

WTNC samples (30×10×5 mm^3; L, R, T) were exposed to the attack of different Basiodiomycete fungi in order to determine their decay resistance. Scot pine samples were exposed to *Coniophora puteana* (CP) (brown rot, temperate strain Bam Ebw 15), beech samples to *Coriolus versicolor* (CV) (white rot, temperate strain CTB 863A).

Sterile culture medium prepared from malt (40 g) and agar (20 g) in deionized water (1 L), was placed in culture flask inoculated with a small piece of mycelium of a freshly grown pure culture and incubated for two weeks to allow full colonization of the medium by the mycelium. The temperate strains were cultivated at 22 ℃ and 70% RH.

In each culture jar were inserted two WTNC samples (only complexes of tannin-hexamine-boron resin and OMMT) and two control samples (figure 5-4). Each sample was placed on a plastic grid to avoid waterlogging and six replicates in total for each group were used. Virulence controls were also performed with eight samples for each brown and white rot respectively. The flasks were incubated for 8 weeks in the climatic conditions described above.

Figure 5-4 Arrangement of fungi test

Once the fungal exposure completed, the mycelium on the samples was removed; and the specimens were weighed (M_3) in order to determine their moisture after fungal degradation (equation 5-7). All performed oven-dry specimens were dried at 103 ± 2 ℃, and the mass loss due to fungal degradation was determined (equation 5-8).

$$\text{Moisture (M,\%)} = \frac{M_3 - M_4}{M_3} \times 100 \quad (5\text{-}7)$$

$$\text{Mass loss (ML,\%)} = \frac{M_2 - M_4}{M_2} \times 100 \quad (5\text{-}8)$$

where M_2 is the oven dry mass (g) prior to test, M_3 is the moistened mass (g) at end of the fungal exposure and M_4 is the oven dry mass (g) after the deteriorated test.

Termite's resistance tests were performed using *Reticulitermes flavipes* (ex. *santonensis*) termites in a non-choice test. Untreated wood of pine and beech was used as virulence control. Prior to the test, the initial mass (M_2) of the samples (30×10×5 mm^3; L, R, T) was determined as explained for the fungal experiments.

Figure 5-5 Layout of termite test

In a 9-cm diameter Petri dish containing 40 g of wet Fontainebleau sand (4 volume sand/1 volume deionized water), a WTNC or a control sample was placed on a plastic mesh to avoid waterlogging (figure 5-6). Fifty workers, two soldiers and two nymphs were introduced in each Petri dish. Six replicates of every series were done. The test devices were held at 27 ℃ and 75% RH in total darkness for four weeks. At the end of the test, the samples were removed and the survival rate of the termite worker was calculated. Damage on the block surfaces was observed visually after stabilization at room temperature. The visual rating was based on the guidelines given by the EN117 (2005) with an adaptation to the size of the samples. Finally, the samples were oven-dried and weighted (M_4), and then the weight loss of the wood sample was calculated (equation 5-7).

5.2.13 Flammability

5.2.13.1 Fire resistant properties conducted by simplified lab-scale apparatus

Fire-simulated lab-scale tests were carried out to evaluate the most important parameters of WTNC samples (only complexes of tannin-hexamine-boron resin and OMMT) regarding fire exposure. In this study, two types of combustion tests were considered: short- and long-time exposure tests.

The short-time exposure fire tests were inspected according to the procedure described in "4.2.10 Short-time exposure lab-scale fire tests".

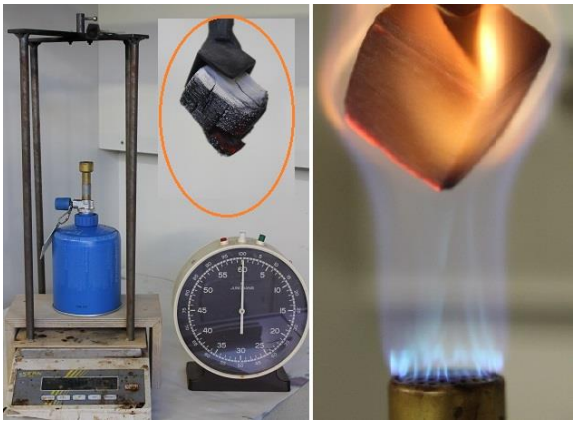


Figure 5-6 Long-time exposure fire test by a simplified lab-scale apparatus

About the long-time exposure fire tests, cubic samples of Scots pine and beech (25×25×25 mm^3; L, R, T) were exposed to direct flame in a lab-made instrument (figure 5-6). The vertex of the sample was exposed to the top of the roaring blue flame of the Bunsen burner (d = 8–10 cm). The weight of the sample was registered every 30 seconds and the weight- loss curve was extrapolated. The test was repeated at least three times for each formulation.

Real-time mass losses of samples after fire test were calculated according to the following equation (5-9):

$$\text{Mass loss } (ML_f, \%) = \frac{W_{af} - W_{bf}}{W_{af}} \times 100 \quad (5\text{-}9)$$

where W_{af} is the initial weight (g) of wood samples before fire test and W_{bf} is the real-time weight (g) of wood samples after fire test.

5.2.13.2 Estimating the fire behavior of WTNC using a cone calorimeter

WTNC samples of Scots pine and beech (only complexes of tannin-hexamine-boron resin and OMMT) were performed the combustion properties on a cone calorimeter. It was recognized worldwide as one of the most acceptable fire testing apparatuses as shown in the figure 5-7. The combustion experiments were performed according to ISO 5660-1 standard procedure on a FTT cone calorimeter (Fire Testing Technology Ltd., UK). The fire scenario was comprised of four steps: ignition, growth, fully developed, and decay. Each specimen of dimensions $100 \times 10 \times 100$ mm^3 (L, R, T) was wrapped in aluminum foil and exposed horizontally to an external heat flux of $50 kW/m^2$ which corresponded to the fully developed step. The back of the samples was insulated with low-conductivity material to reduce heat losses to the sample holder. When ignition flame occurred, the time was recorded and the spark power and the igniter were removed. If the flame went out after removing the spark power, the igniter was re-inserted within 5 s and then the spark was maintained until test completion. The sample and sample holder were removed after the collection of all data during the test. An insulation material was situated above the mass measurement device. During the test, the following parameters were determined: time to ignition (TTI), heat release rate (HRR), peak HRR (PHRR), smoke production rate (SPR), and carbon monoxide yield. Average values of the parameters were calculated from the three tests for each formulation.

Figure 5-7 Experimental set-up of the cone calorimeter: left - schematic of Cone, right - close-up of burning specimen in the cone calorimeter

5.2.14 Behaviour of thermal degradation

The samples from WTNC and control specimen of Scots pine and beech used previously for FTIR and XRD were obtained for thermal analysis.

5.2.14.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) measurements were carried out in the thermogravimetric analyzer (Pyris 6, Perkin-Elmer, USA). The analysed sample weights varied from 2 to 10 mg. Analysis was carried out with a nitrogen flow rate of 20 ml/min. Ceramic crucibles loaded with WTNC powders were placed inside the TG apparatus where the weight was constantly measured. The temperature was varied from 0 to 800 ℃ and the heating rate from 10 ℃/min. A temperature program consisting of a dynamic heating period followed by an isothermal heating period was applied. During the dynamic heating period the biomass was thoroughly dried. All samples were analysed three times. In thermogravimetry, analysis data were obtained with respect to weight loss versus reaction temperature or time.

5.2.14.2 Simultaneous differential scanning calorimetric and thermogravimetric analysis

Simultaneous thermogravimetry were also used to determine the thermal characterization of WTNC. The techniques of differential scanning calorimetric (DSC) and TGA were used simultaneously to measure the change in sample mass with temperature as well as changes in enthalpy that occur during pyrolysis. The simultaneous TGA-DSC apparatus of STA 449 F3 Jupiter® (NETZSCH, Germany) was used in this process. To achieve good baseline stability, it is important that platinum crucibles are conventionally cleaned by boiling the sample containers in water, soaked in 10% hydrochloric acid, rinsed with water and baked in the muffle furnace at 900 ℃ for four hours. Calibration of simultaneous TGA/DSC apparatus was performed in four steps with empty pan and standard sapphire disc. The four calibration subroutines of TGA weight, DTA baseline, DSC heat flow and temperature were carried out before an actual measurement on the sample. Samples were contained in a platinum crucible alumina crucible. Series of experiments were performed using 10±2 mg sample size. The atmosphere consisted of flowing protective inert atmosphere of N_2 at a rate of 50 ml/min. TGA, DTA and DSC curves were obtained by heating samples from room temperature to 900 ℃ with a ramp rate of 10 ℃/min. All samples were analysed three times. Furnace control employed algorithms enabling closely occurring decomposition events to be separated. Both DSC and TGA curves were corrected by subtraction of a baseline which was run under identical conditions as DSC–TGA measurement with residue of samples in the crucible. The Netzsch Proteus® Thermal Analysis Software was used for DSC and TGA data analysis. Thermal decomposition profiles were used to interpret and compare thermal stability.

5.3 Results

5.3.1 FTIR analysis

Firstly, the infrared spectra of purified MMT and OMMT were shown in figure 5-8 to verify the organ-modified efficacy. The FTIR spectra of Na-MMT and OMMT showed the presence of bands at about 3600 and 1100 cm^{-1} which are the typical hydroxyl group bands of MMT. Compared with the FTIR spectra of purified MMT, the absorption band at 3412 cm^{-1}, corresponding to –OH stretching vibration of H_2O of MMT, weakened and shifted to the lower wave number 2919 cm^{-1}. The characteristic absorption bands at 2920 cm-1 and 2850 cm-1 respectively corresponded to C–H asymmetric stretching mode and symmetric stretching mode of alkyl chains (Venkataraman and Vasudevan 2000, Zhao et al. 2003) were observed on the spectra of surfactant-modified MMT. The band shift from lower frequency to higher frequency meant that the number of highly ordered (all-trans) conformers of alkyl chain decreases whereas guache conformers increases. The spectrum of OMMT had some spectral features similar to that of MMT. Nevertheless, the presence of the CTAB cations demonstrated the bands at 1486 and 1468 cm^{-1} (asymmetric C–H bending vibrations of both –CH_3 and –CH_2 groups), a band at 1416 cm^{-1} (symmetric (CH_3)–N bending vibration) (Madejova 2003). The rocking mode at 720 cm^{-1} was diagnostic of packing arrangements in alkyl chain assemblies (Zhu et al. 2005). These broad singlets related with either a liquidlike molecular environment and/or disordered hexagonal subcell packing, where the alkyl chain rotated freely around its long axis. Compared with the FTIR spectra of purified MMT, the absorption band of –OH bending vibration of H_2O of MMT (1635 cm^{-1}) moved to 1639 cm^{-1}.

Simultaneously, the intensity of this absorption band decreases, which indicated the H_2O content reduced with the replacement of the hydrated cations by surfactant cation ions. This observation showed that the surface properties of MMT had been changed from hydrophilic to hydrophobic by modifying it with surfactants (Wang and Wang 2008).

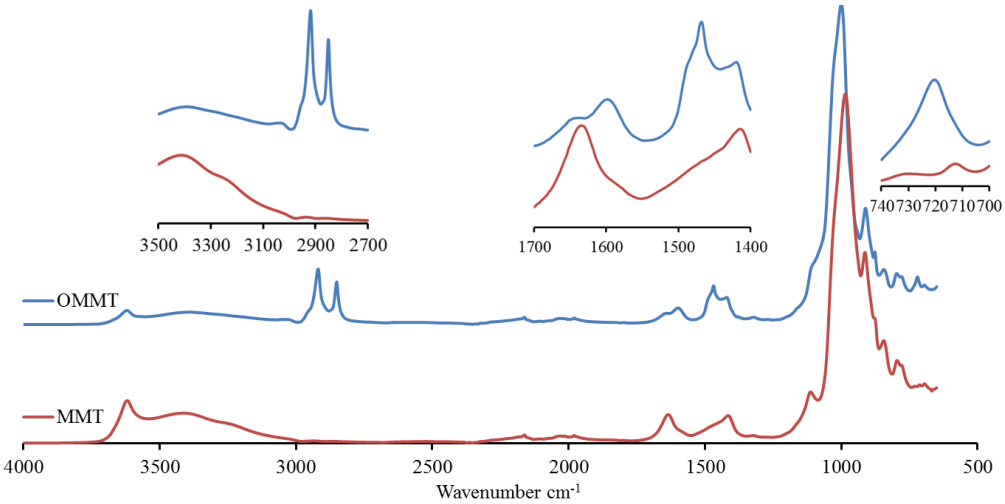


Figure 5-8 FTIR spectra of purified MMT and OMMT

The FTIR results of pine and beech WTNC via tannin resin with and without hexamine were showed in figure 5-9 and 5-10, respectively.

From figure 5-9 and 5-10, it can clearly be seen that the absorption spectra of WTNC via tannin resin with and without hexamine were nearly similar, excluding the intensity of peaks. A new absorption band at 3621 cm^{-1} is observed in pine and beech WTNC with compare to wood controls. It can be seen that absorption spectrum belt of 3200cm^{-1}~3500cm^{-1} corresponding to hydroxyl vibration is broader obviously, but the absorption intensity declines. Meanwhile, the

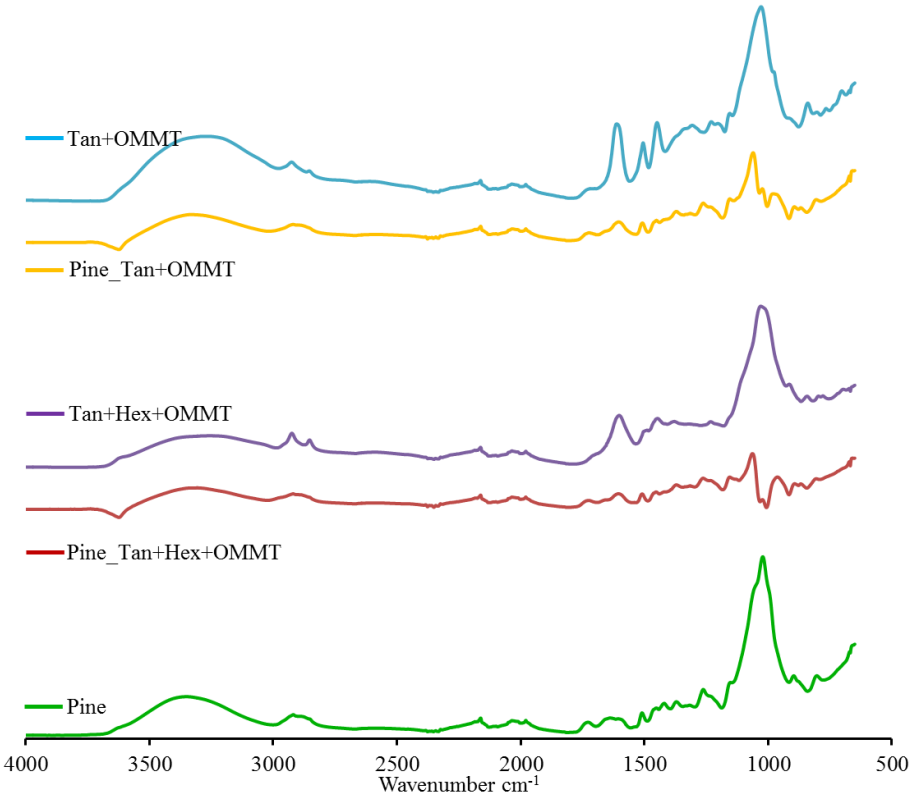


Figure 5-9 FTIR spectra of pine WTNC

absorption peaks for the –OH stretching vibration near 3300 and 1590 cm^{-1} were augmented because of the associated hydroxyl group increase in pine and beech wood. According to FTIR spectroscopy, the ordering degree of clay mineral was best characterized by the Si–O–Si group belonged to MMT at the peak of 1040 cm^{-1}, which corresponded to well-ordered montmorillonite. This absorption band can be inspected in the spectra of WTNC, for both pine and beech.

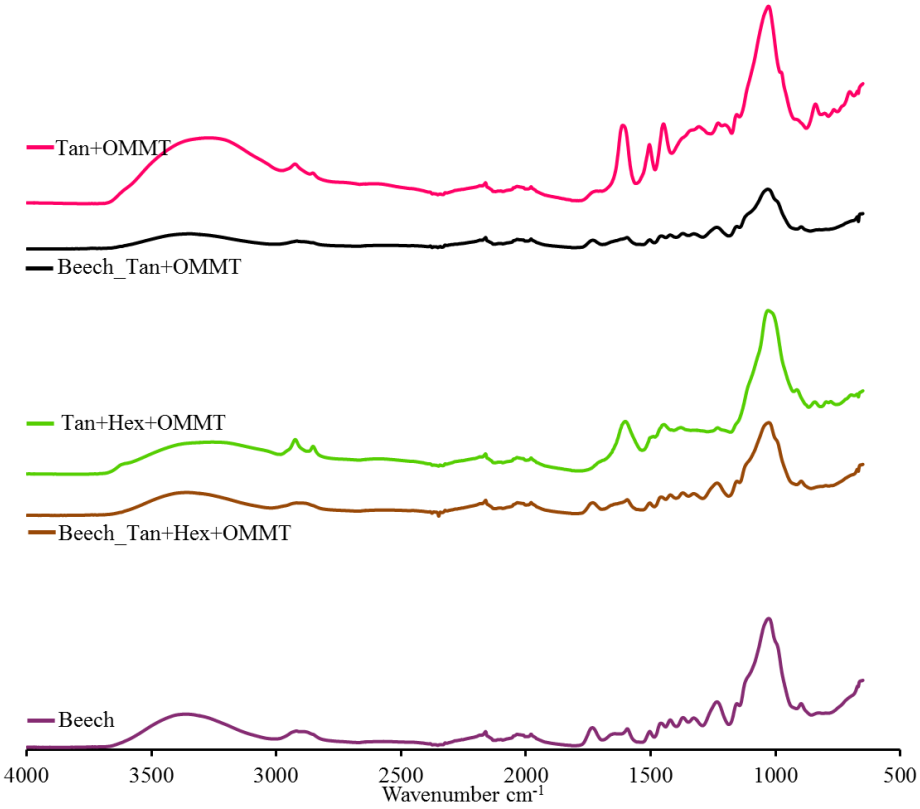


Figure 5-10 FTIR spectra of beech WTNC

5.3.2 XRD analysis

When compared to pristine MMT (*d*-spacing value of 1.56nm) in figure 5-11, OMMT showed increased *d*-spacing values to 3.29nm, which suggested a wider interlayer distance of OMMT than MMT. Therefore, the long-chain alkylammonium ions had been intercalated between the layers during the cation-exchange process adopting a pseudo-trimolecular arrangement (Lagaly 1994). Likewise, the augment was similar from nanoclay composites mixed with tannin resin, which indicated tannin polymer chain had intercalated into the layer of OMMT and penetrated into the hydrophobic OMMT gallery spacing. The conclusion based on the FTIR results of MMT and OMMT, that modification of MMT with CTAB cations was successful, was also fully supported by the XRD analysis.

From figure 5-12 and 5-13, there was nearly no distinct difference to XRD spectra of pine and beech WTNC, moreover, which were also similar with control excluding the intensity of peak. With the incorporation of OMMT and tannin resin (with and without hexamine) into wood, a shifting of crystalline peak of wood from higher to lower angle as well as disappearance of (001) crystal diffraction peak of nanoclay was observed. After OMMT being introduced into wood, the most significant diffraction peak of the cellulose crystal diffraction (the reflection

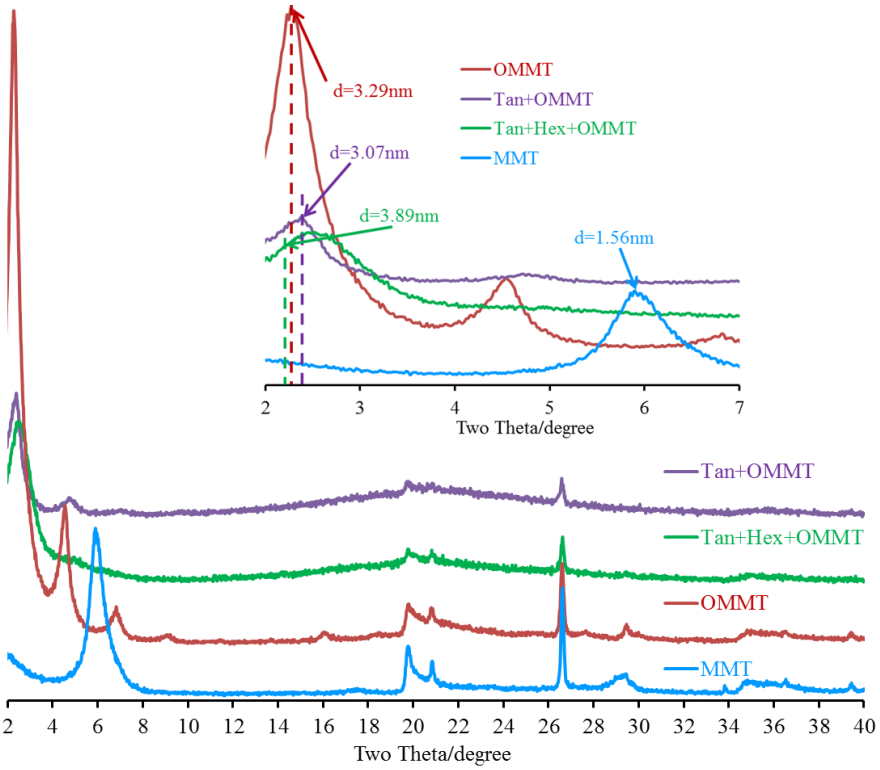


Figure 5-11 The X-ray diffraction spectra of MMT, OMMT, complex of OMMT-tannin resin with and without hexamine

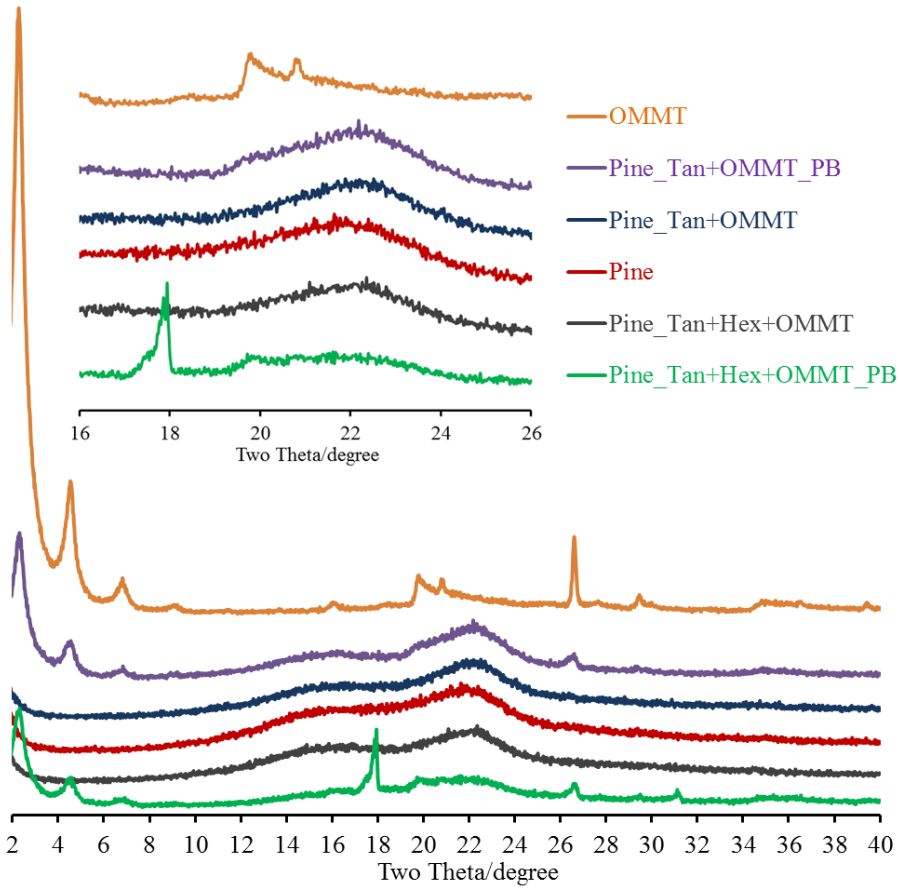


Figure 5-12 The X-ray diffraction spectra of OMMT, pine WTNC via tannin-boron resin with and without hexamine, pine control, complex of OMMT-tannin resin with and without hexamine

002) near 21.6 ° gradually passivated in contrast to that of wood control (Cave, 1997). Furthermore, the XRD patterns of simply physical blend for wood powder, tannin resin and OMMT were depicted the curve of the characteristic diffraction peak of OMMT at 2.25 of two theta. But this peak of WTNC curve disappeared, which denoted that the MMT gallery space was greatly expanded, or MMT nanolayers were exfoliated free.

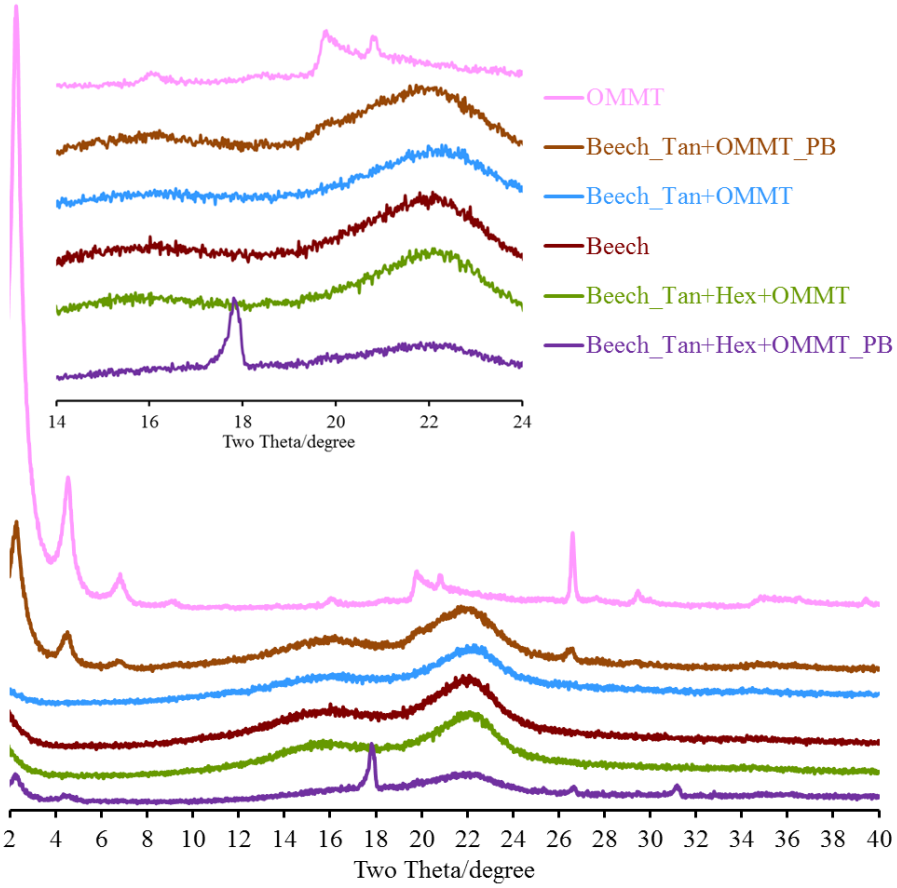


Figure 5-13 The X-ray diffraction spectra of OMMT, beech WTNC via tannin-boron resin with and without hexamine, beech control, complex of OMMT-tannin resin with and without hexamine

5.3.3 Complex solution retention in treated specimens

In this study, the retentions of all treated solutions in wood were presented in table 5-2 and 5-3. Pine sapwood and beech are always chosen because they are very easily impregnated. Thus, the retention of the solutions will give information on the ability of the impregnation solutions to treat the wood.

Two tables can generally be concluded that samples of Scots pine treated with all solutions achieved the higher total retentions than that of beech.

In table 5-2, when the similar treated solution was introduced into wood, the dimension of sample from the same wood species could influence the retention. The less longitudinal dimension to the specimen of similar surface can seemly bring about a higher retention.

In table 5-3, by comparison, the complexes of tannin-hexamine-boron resin and OMMT can attain a higher retention to the same samples. There appeared to be some effects of different impregnated solution on the retention since these results were available for all solutions evaluated (Table 5-3).

Table 5-2 Retention of specimens to other experiments excluding biological tests with complexes solution of tannin-hexamine-boron resin and OMMT

Assay and dimension (L, R, T; mm)	Retention of different additive and wood species (SD) (kg/m^3)							
	Pine				Beech			
	Total	Tan.	BA	MMT	Total	Tan.	BA	MMT
Compression + Hardness, 60×20×20	77.00 (7.98)	50.77 (5.26)	2.76 (0.29)	20.17 (2.09)	71.83 (3.78)	47.37 (2.49)	2.57 (0.13)	18.82 (0.99)
Gluing + Wettability, 80×20×5	86.96 (3.01)	57.34 (1.99)	3.11 (0.11)	22.78 (0.79)	74.09 (3.31)	48.85 (2.18)	2.65 (0.12)	19.41 (0.87)
Dimension stability, 10×20×20	98.07 (1.02)	64.67 (0.68)	3.51 (0.04)	25.70 (0.27)	86.45 (3.09)	57.00 (2.03)	3.10 (0.11)	22.65 (0.81)
Short-time combustion, 50×25×15	81.75 (6.27)	53.90 (4.13)	2.93 (0.22)	21.42 (1.64)	57.55 (4.47)	37.95 (2.95)	2.06 (0.16)	15.08 (1.17)
Long-time combustion, 25×25×25	81.92 (19.45)	54.01 (12.82)	2.93 (0.70)	21.46 (5.10)	78.70 (4.11)	51.89 (2.71)	2.82 (0.15)	20.62 (1.08)
Cone test (OMMT), 100×10×100	76.71 (3.86)	50.58 (2.54)	2.75 (0.14)	20.10 (1.01)	69.26 (3.46)	45.67 (2.28)	2.48 (0.12)	18.15 (0.91)
Cone test (No OMMT), 100×10×100	66.14 (0.69)	43.80 (0.46)	2.38 (0.02)	0	53.52 (1.77)	35.45 (1.17)	1.93 (0.06)	0

Table 5-3 Retention of biological specimens in all formulations including OMMT

Formulation 30×10×5 mm^3	Retention of different additive and wood species (SD) (kg/m^3)							
	Pine				Beech			
	Total	Tan.	BA	OMMT	Total	Tan.	BA	OMMT
BA + OMMT	26.02 (1.06)	0	3.13 (0.13)	22.89 (0.93)	23.31 (1.72)	0	2.80 (0.21)	20.51 (1.51)
Tan. + BA + OMMT	90.09 (3.77)	59.40 (2.49)	3.23 (0.14)	23.60 (0.99)	61.68 (7.06)	40.67 (4.66)	2.21 (0.25)	16.16 (1.85)
Tan. + BA + Hex. + OMMT	122.82 (10.33)	58.03 (4.88)	3.15 (0.27)	23.06 (1.94)	89.25 (10.30)	42.17 (4.87)	2.29 (0.26)	16.76 (1.93)

5.3.3 Morphological studies

Actually, the microscopic investigation to wood samples treated with the complex of OMMT and tannin-boron resin with hexamine and no hexamine had been performed. As no difference in two treatments was observed, only the treatment with hexamine was reported here.

The penetration of complexes with the same formulation and the same impregnation conditions in pine and beech was investigated by some morphological studies. From figure 5-14 and 5-15, complexes of tannin and OMMT were observed on the cell walls of pine and beech.

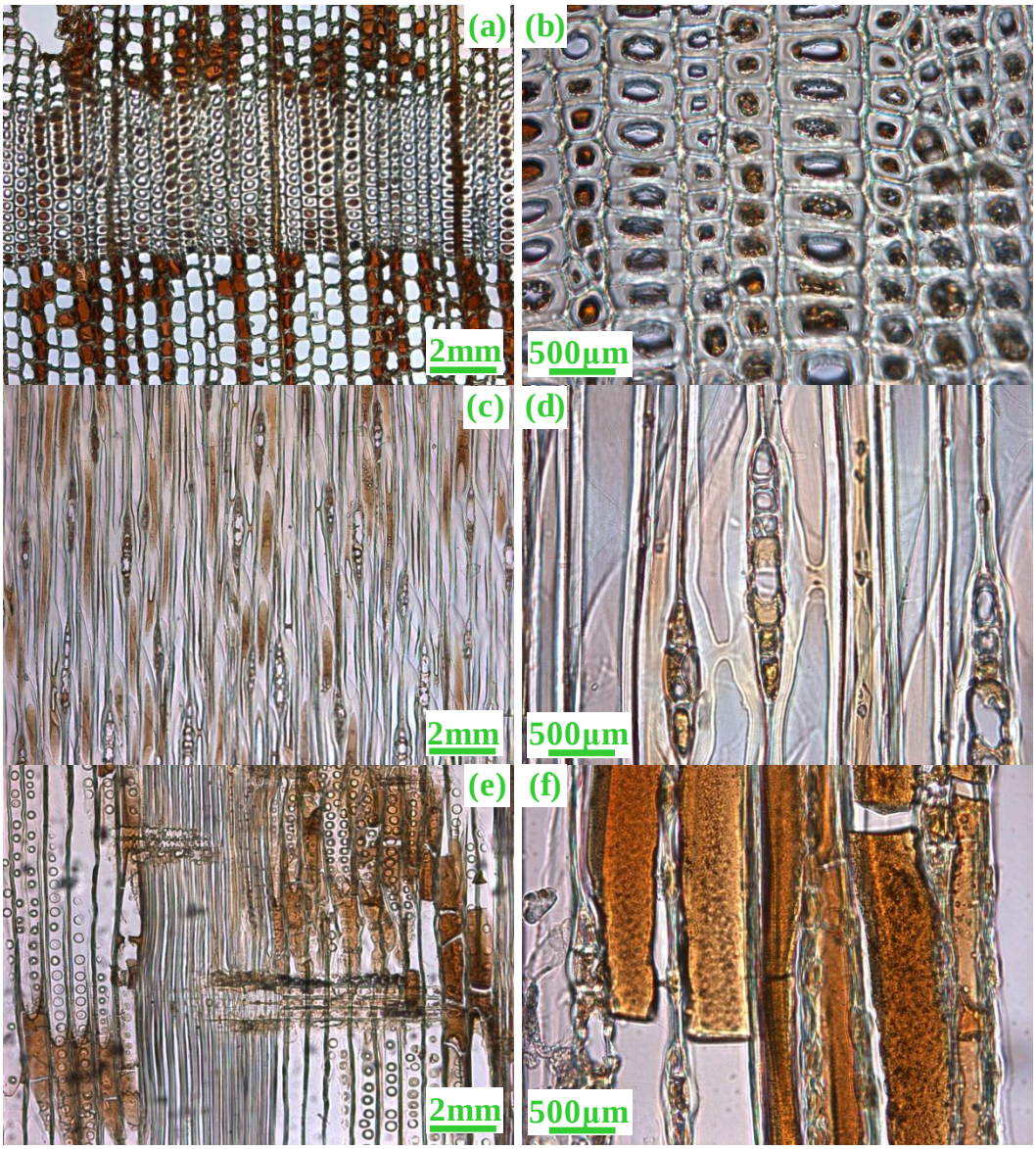


Figure 5-14 Microscope images of pine WTNC: the magnification of left image was at ×10, the magnification of right image at ×40; a and b was transversal section, c and d was tangential section, and e and f was radial section.

Microscope pictures of three sections of pine WTNC were reported in figure 5-14. Tracheids are penetrated. Full impregnation can be observed for the most part of the latewood, while partial impregnation affects the earlywood. Especially, some complexes of tannin and OMMT can be found in lumen and wall of tracheids. In the adjacent position with parenchyma rays, tracheids were richly impregnated. Nearly all parenchyma rays were entirely filled by the impregnation solution. In the resin canals, any solution penetration was not found. It was difficult that solutions passed through bordered pits, where nothing was remained.

The microscopic investigation of beech is depicted in figure 5-15. The impregnation took place almost exclusively across the longitudinal direction through the large and easily accessible vessels. In the tangential and radial sections, it was possible to emphasize that not all the vessels were entirely filled due to the dimensions of the cells. Likewise, parenchyma cells were also penetrated in beech WTNC. Most of rays were filled by complexes of tannin and OMMT. In the middle of the specimen, only the larger vessels were impregnated due to the blocking effect of bigger tannin oligomers.

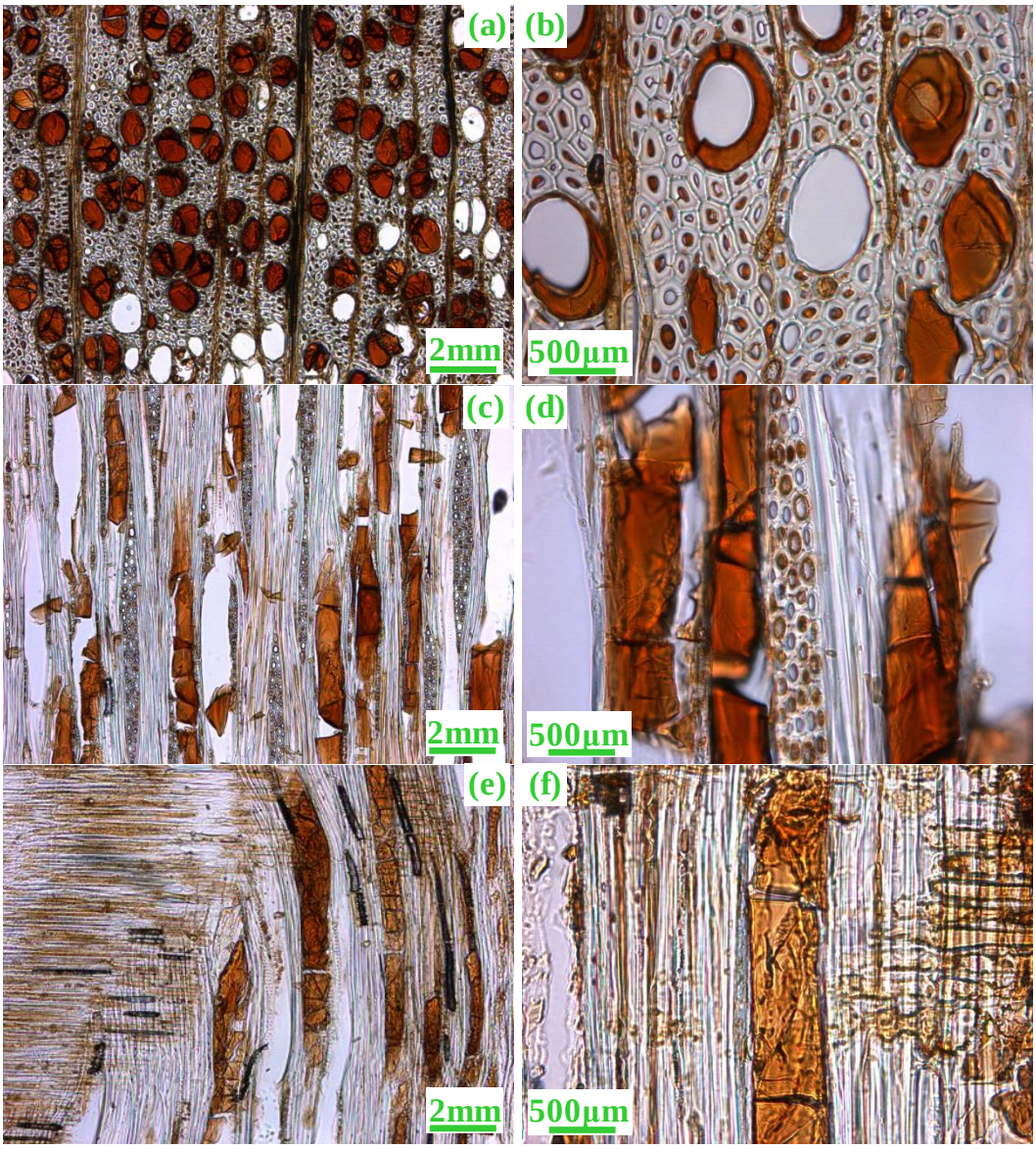


Figure 5-15 Microscope images of beech WTNC: the magnification of left image was at ×10, the magnification of right image at ×40; a and b was transversal section, c and d was tangential section, and e and f was radial section.

Some SEM images of pine and beech WTNC were shown in figure 5-16. Much granular material was gathered in the cell lumen and on the cell walls (indicated by red signs). In figure 5-16b, a ×1500 SEM image clearly presented OMMT to immerse tannin polymer, which were filled in the cell lumen of pine timber. Figure 5-16 a and c indicated the trace of OMMT on the cell wall. In the wood ray, OMMT can be detected, which were just filled into a cell of wood ray.

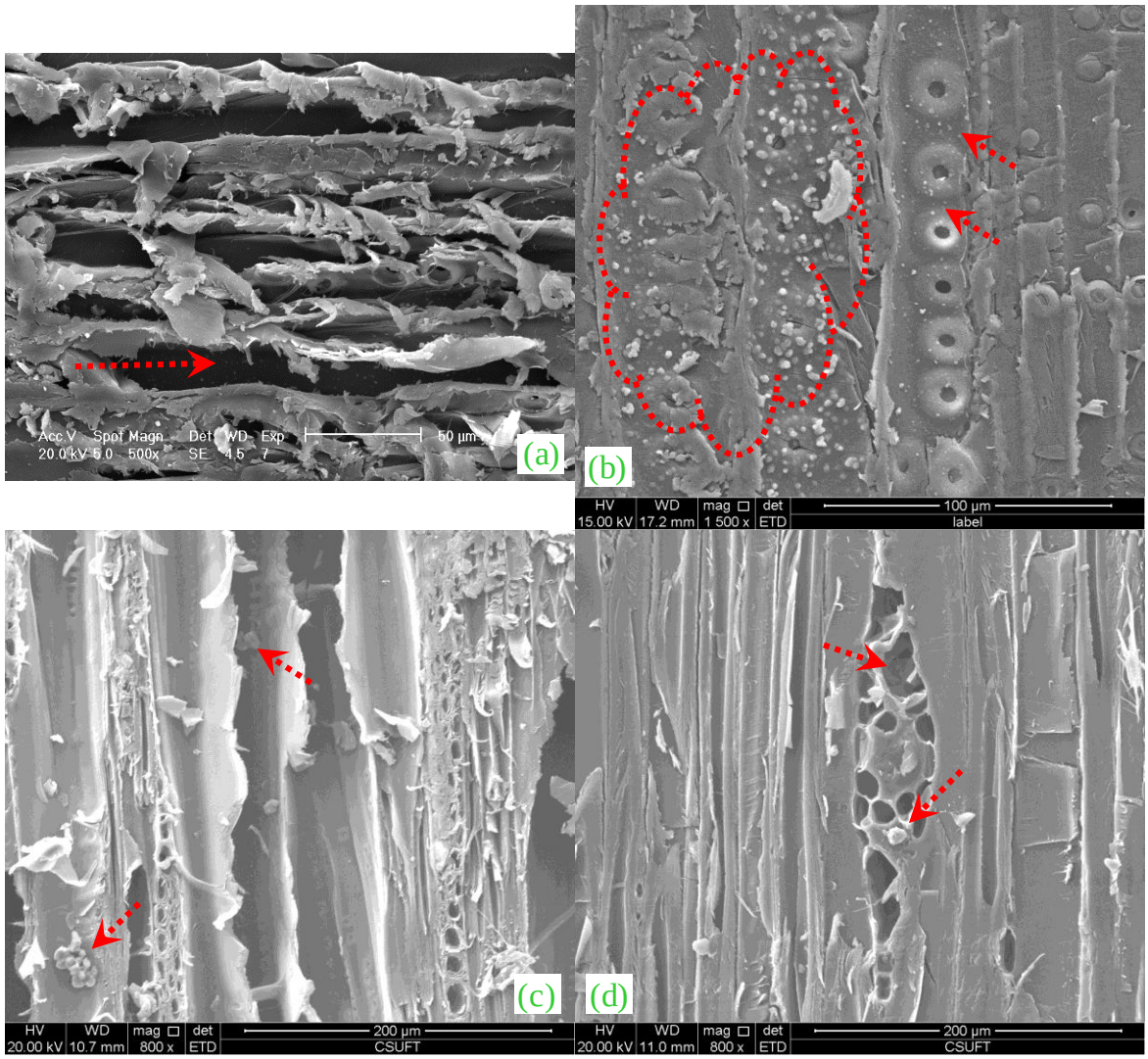


Figure 5-16 SEM of pine and beech WTNC: a and b pine WTNC, c and d beech WTNC

5.3.4 Mechanical property----axial compression strength

Figure 5-17 represented the strength performance in compression resistance of pine and beech WTNC. The most immediate result was that an improvement in compression resistance

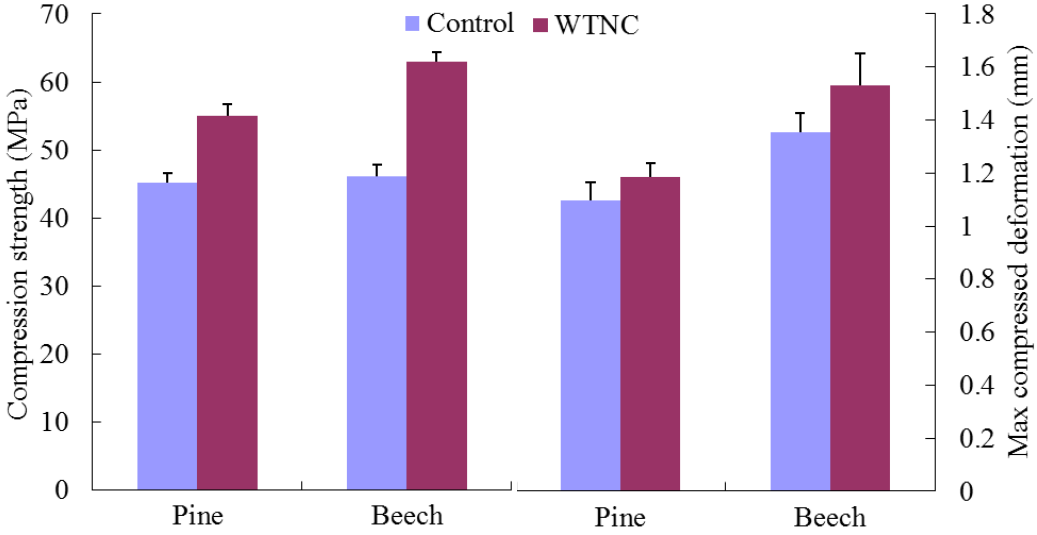


Figure 5-17 Compression strength and max compressed deformation of WTNC

occurs for each species WTNC: pine WTNC specimens achieved an improvement in compression strength of up to 21.6%; beech WTNC specimens got an improvement in compression strength of up to 36.3%. In addition, permanent deformation also proved the effect of tannin-OMMT complexes, which formed when stiffness of wood had arrived at the high point to break. The max compressed deformation of pine and beech WTNC was kept up to 8.2% and 13.0%, respectively.

5.3.5 Surface properties

5.3.5.1 Hardness

The WTNC samples always increased their hardness after impregnating into complexes of tannin and OMMT and also their resistance to mechanical surface solicitations is upgraded. The average Brinell hardnesses of pine and beech WTNC specimens were respectively 19 MPa and 30 MPa and distinctly optimal to control specimens. Based on the results (figure 5-18a), the tangential and radial surface hardnesses of pine wood is similar with and without nano-modifications. However, It was determined that the induction of complexes of tannin and OMMT had more effects on hardness in different transverse section of beech wood than pine wood. To beech wood, the tangential surface hardness is higher than the radial surface hardness. Likewise, the diameter of residual indentation also proved the aforementioned conclusion (figure 5-18b).

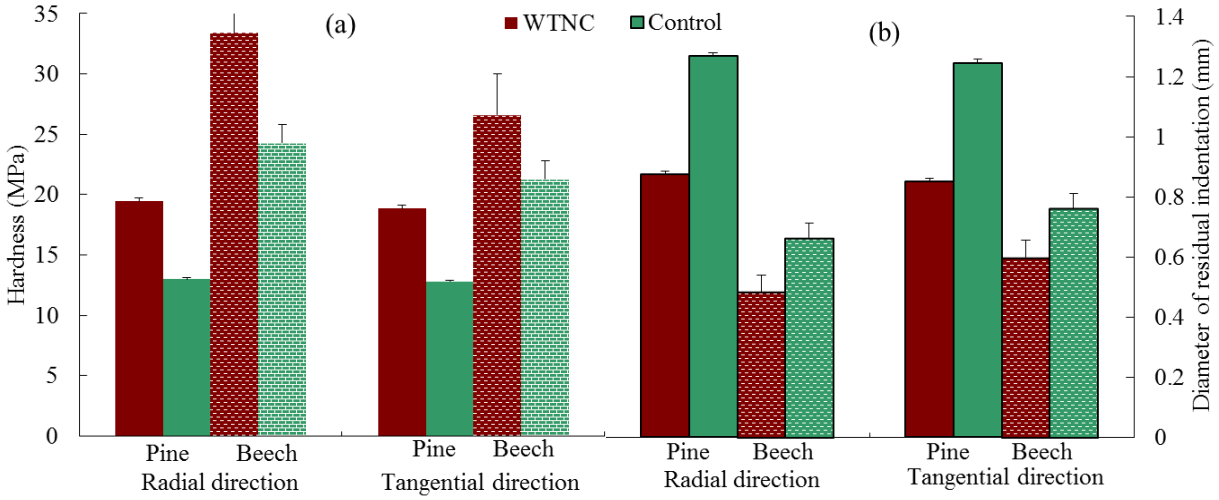


Figure 5-18 Hardness of WTNC: (a) value of Brinell strength for WTNC and control, (b) diameter of residual indentation for WTNC and control

5.3.5.2 Bonding potential

An important property of WTNC surface was analyzed to investigate the bonding potential. The test was performed with the water-based vinyl glue to simulate several possible exterior applications. The results of the shearing tests related to treated wood with complexes of tannin and OMMT were shown in Table 5-4. In all cases, the failure was into the wood, except for treated beech, for which the failure was into the glue line.

In the case of beech WTNC, the shearing resistance tests actually showed the strength of glueline when these surfaces of treated samples had completely exposed. However, in other cases the shearing tests showed the strength of wood when those surfaces of samples still remained sufficiently agglutinate.

Table 5-4 Gluing properties of pine and beech WTNC surfaces

Wood species	Treatment	Wood failure (%)	Shearing resistance (MPa)
Pine	Treated	100(0)	10.66(1.95)
	Control	100(0)	10.81(2.86)
Beech	Treated	0(0)	13.52(1.12)
	Control	100(0)	14.60(2.35)

Notes: Standard deviations shown in parentheses.

5.3.5.3 Wettability

The inducted complexes of tannin and OMMT affected surface wettability, as determined by contact angle measurements. The contact angles of water droplet acquired from using the mean method were shown in table 5-5. The contact angles of water on controls hardwood and softwood were not much different. For the surfaces of wood samples with and without treatment, significant difference was observed in contact angle measurements. However, beech improved by nano-modification formulation was given more contact angle than pine.

Table 5-5 Contact angles of WTNC samples

Sample classification	Pine control	Pine WTNC	Beech control	Beech WTNC
θ (degree)	59.14(6.38)	73.73(4.33)	55.06(5.62)	77.11(2.32)

Notes: Standard deviations shown in parentheses.

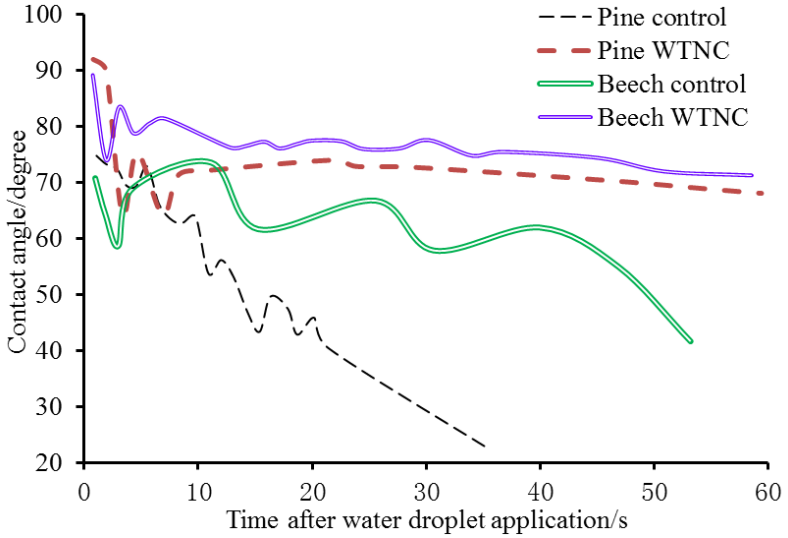


Figure 5-19 Contact angle changes as a function of time on WTNC surface

Figure 5-19 showed the experimental data of the contact angle decrease as a function of time for the specimen surface of WTNC and control. Each data pointed on a mean value curve was the average of 20 measurements on pine or 26 measurements on beech. The variation in the results of controls was relatively large, as can be expected with a heterogeneous material such as wood. The initial contact angle for WTNC and control varied between 66 and 90 ° and the maximum value between 75 and 94 °. Beech surfaces had lower initial values and higher maximum values after 2 seconds than pine, no matter WTNC and control. It was apparent that the instantaneous wettability of WTNC was improved more than the relative control. For

control's surfaces, the instantaneous contact angle continued to decrease throughout the whole measurement period, especially pine wood. However, the instantaneous contact angle of WTNC nearly stabilized after 10 seconds.

5.3.6 Evaluation of water absorption

Water absorption levels (WA) of WTNC were given in figure 5-20. Water repellents reducing effect on water absorption levels of wood was shown in table 5-6. In WTNC and control samples, water absorption increased with an increase in time of immersion. Control samples absorbed more water than WTNC samples excluding beech WTNC after five hours. About the WRE values for control and WTNC samples in water at room temperature, there was a remarkable improvement in WRE values for pine WTNC, however, the WRE values at 30 and 78 h was particularly negative for beech WTNC.

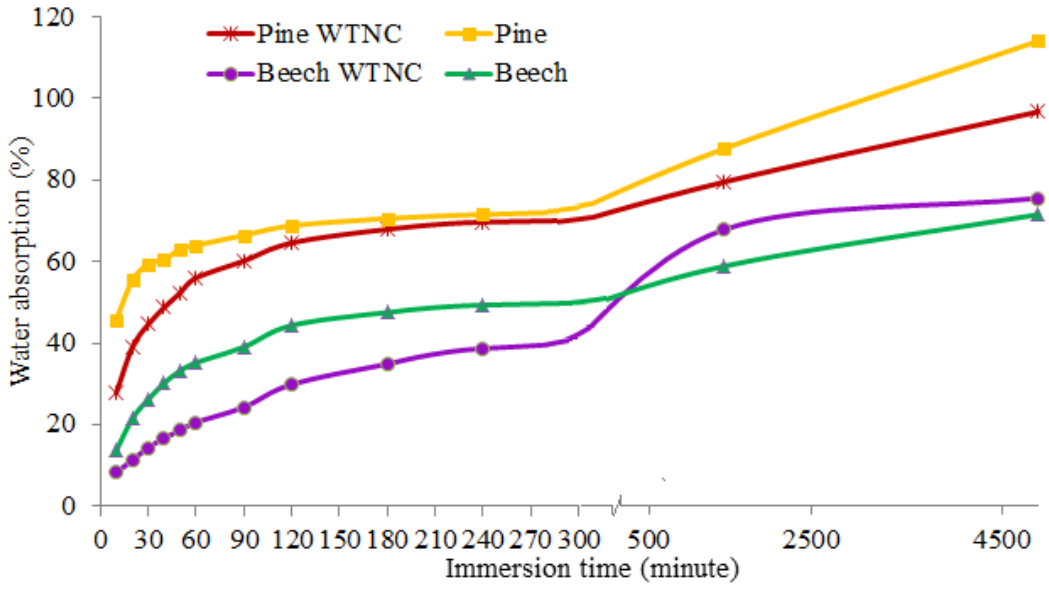


Figure 5-20 Water absorption tests of wood samples

Table 5-6 Water-repellent effectiveness of WTNC

Time (minute)		10	20	30	40	50	60	90	120	180	240	1800	4680
WRE (%)	Pine WTNC	39.43	29.58	24.90	19.34	17.12	12.52	9.44	6.14	3.78	2.62	8.65	14.32
	Beech WTNC	39.20	47.44	45.06	44.72	43.77	41.54	37.76	32.62	26.63	21.56	-13.60	-5.09

5.3.7 Analysis of dimensional stability

5.3.7.1 Dimension swelling in the water

The effect of swelling in liquid water at room temperature for WTNC and control samples for different time periods is shown in figure 5-21. Tangential and radial section of pine WTNC samples were found to swell less compared to untreated samples in initial one hour. But tangential and radial section of beech WTNC resisted more effective deformation in the water than control until respectively 30h and 6h.

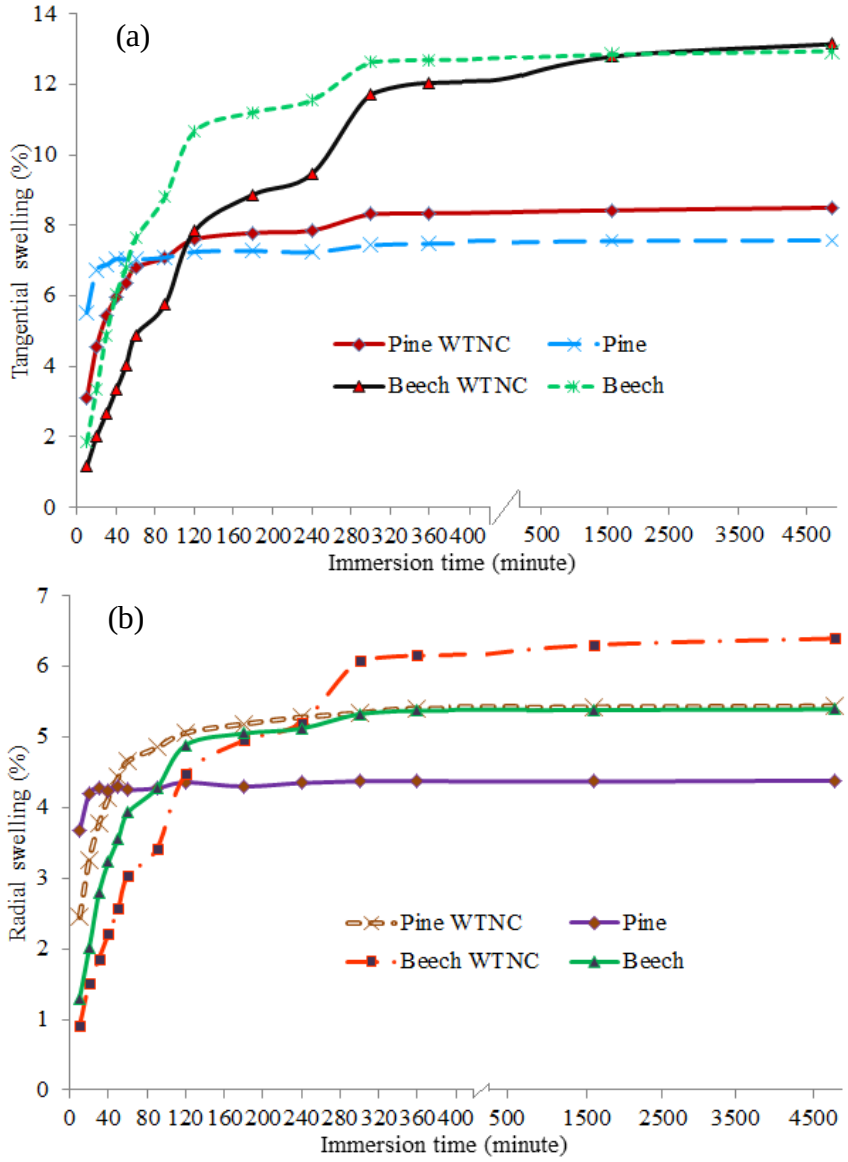


Figure 5-21 Tangential (a) and radial (b) swelling of WTNC in the water

5.3.7.2 Dimension stability in the vapor

The results showing the effect of swelling and shrinkage in water vapor at 20 ℃ and different relative humidities were respectively presented in figure 5-22 and 5-23, likewise, the dimensional changes versus moisture content of samples were indicated in the same figures. As not expected, WTNC samples cannot show more reduction in the radial and tangential swellings and shrinkages. The swelling behaviours of pine and beech WTNC samples were very similar, and in particular the beech WTNC samples indicated nearly same trend of tangential swelling compared to the controls. In the radial direction, the swelling was significant even with a low humidity level, while in the tangential direction notable differences in swelling of pine and beech WTNC took place at only 90% relative humidity. The ratio between the radial and tangential swelling (swelling coefficient) appeared that for untreated pine and beech wood these coefficients were always around 0.64 and 0.51, and for pine and beech WTNC the ratio was around 0.72 and 0.54. This means that the internal strain of the pine WTNC sample was around 8% higher than the control, and there is little difference between the ratios of beech WTNC and control.

Averages for tangential and radial shrinkage of pine and beech WTNC depicted the total shrinkage at 20 ℃ and different relative humidities. The shrinkages of WTNC were all significantly greater than controls. The shrinkage coefficients of WTNC were higher than controls. In current studies, the ratios of radial and tangential shrinkage in pine and beech WTNC/control were respectively: 0.71, 0.63, 0.67 and 0.57.

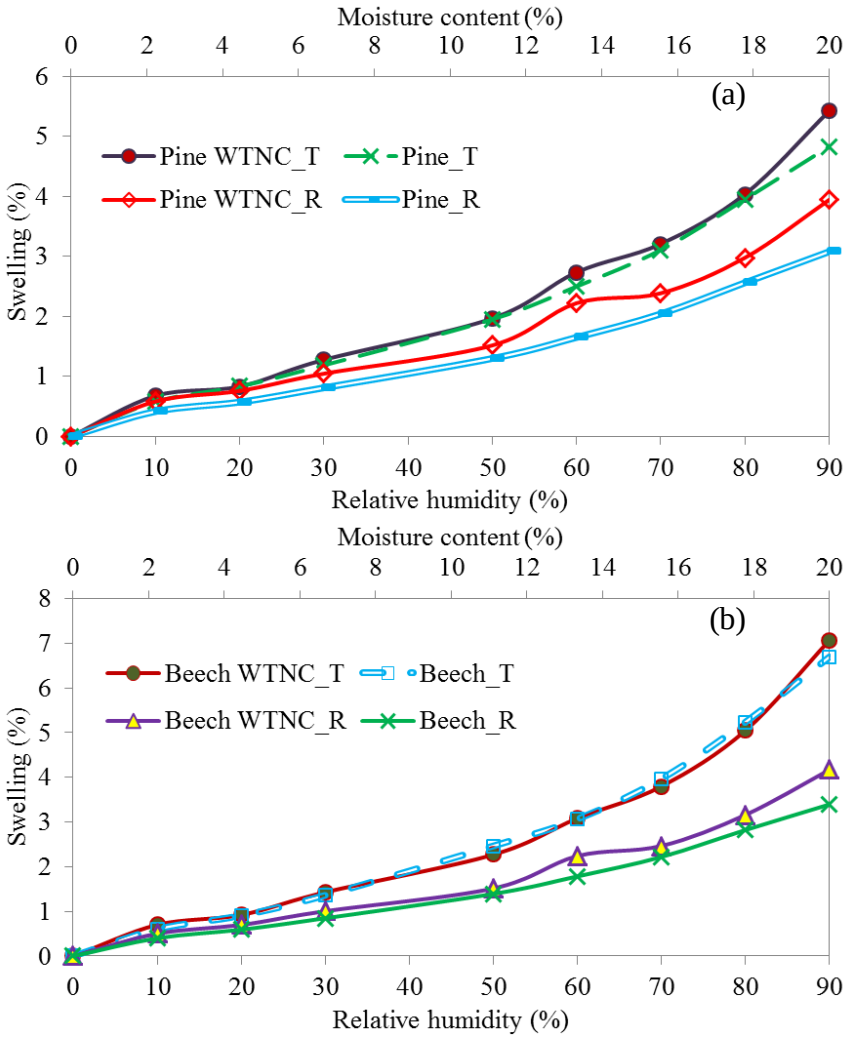
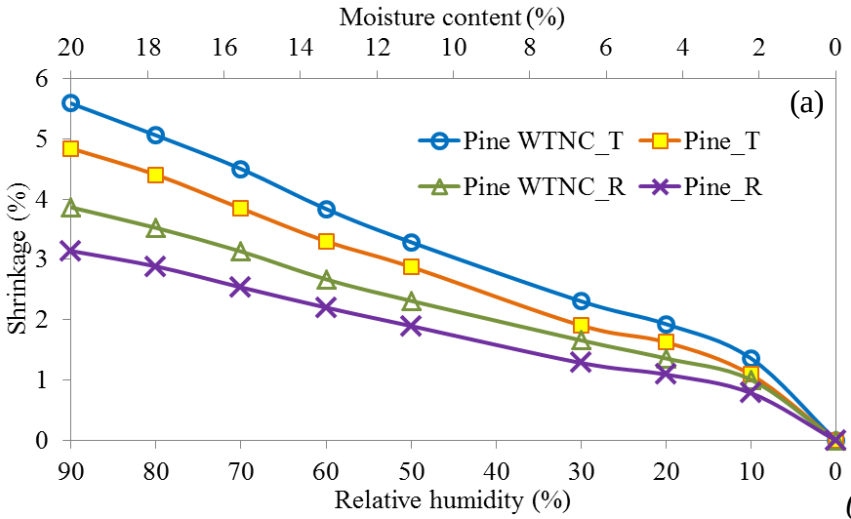


Figure 5-22 Tangential and radial swelling of pine (a) and beech (b) WTNC at 20 ℃ and different relative humidities



(Continued)

Figure 5-23 *(Concluded)*

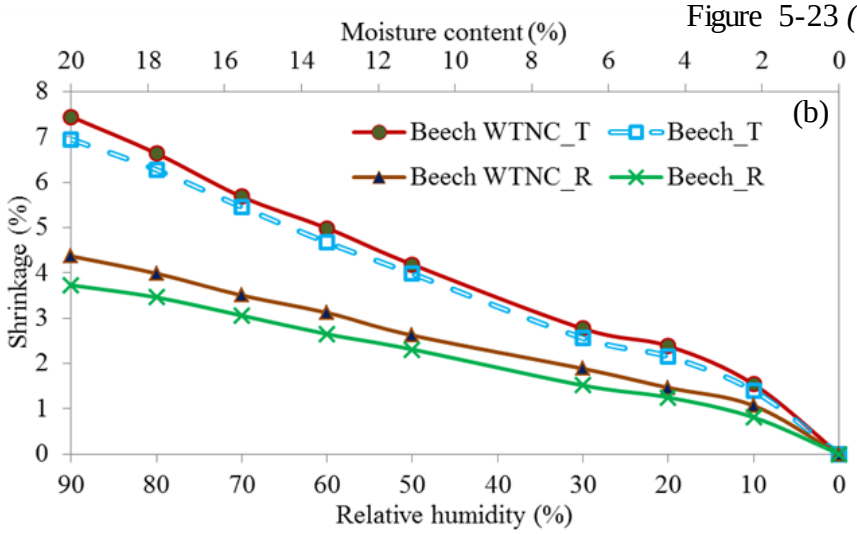


Figure 5-23 Tangential and radial shrinkage of pine (a) and beech (b) WTNC at 20 ℃ and different relative humidities

The shrinkages of WTNC and control after one-month immersion water were investigated and compared to one without being submerged. The results were indicated in figure 5-24. It was clear that the shrinkage of samples without the immersion water were slightly less that correspondent ones in the immersion water. After the immersion water, the difference between radial and tangential shrinkage also increased little: respectively 1.4% (pine WTNC), 6.0% (pine control), 4.7% (beech WTNC) and 8.77% (beech control) comparing with the aforesaid shrinkage ratio.

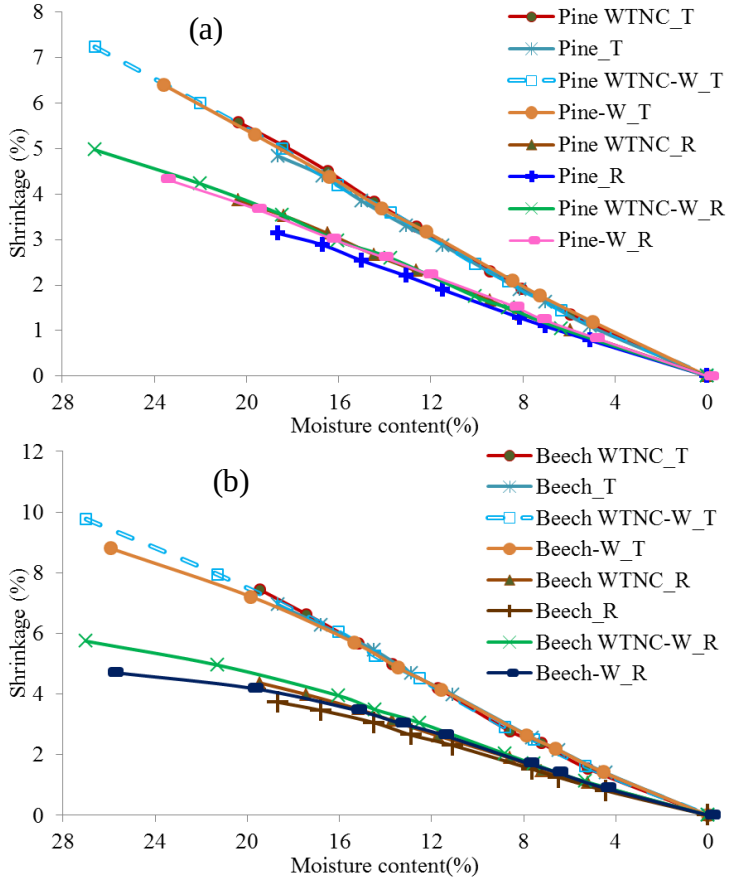


Figure 5-24 Comparison of shrinkage at 20 ℃ and different relative humidities: (a) Pine wood and (b) Beech wood with/without being submerged

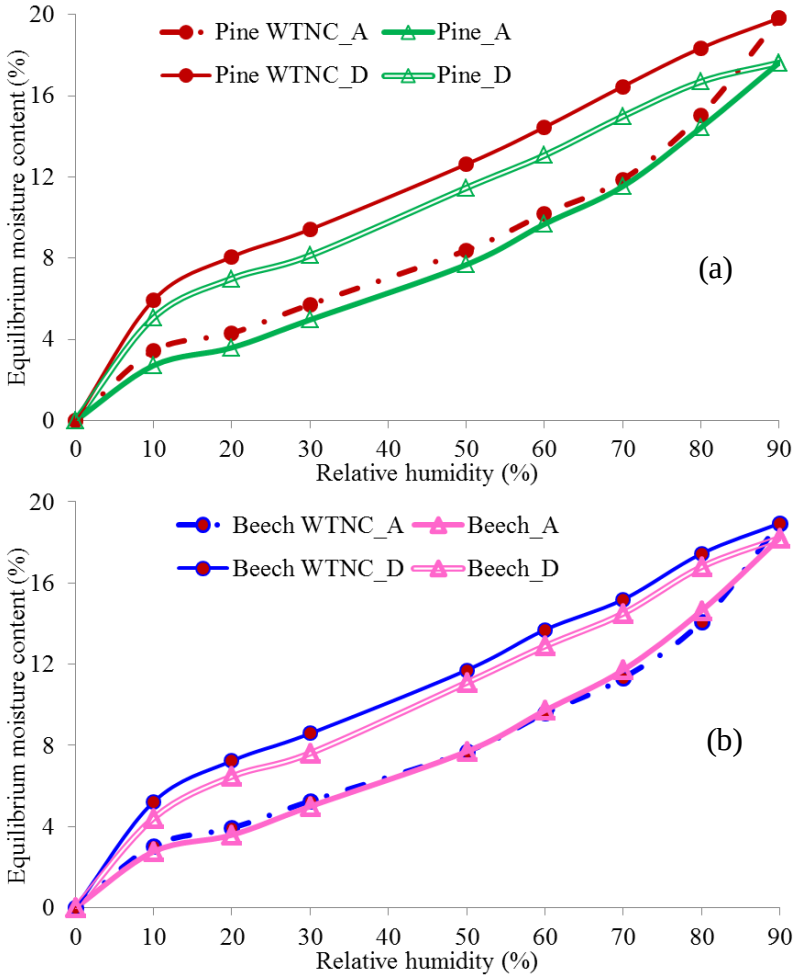


Figure 5-25 Adsorption isotherms and desorption isotherms for (a) pine and (b) beech WTNC and control (a) pine and (b) beech samples (A-Absorption, D- Desorption)

Figure 5-25 showed the for WTNC and control specimens. These isotherms can be classified as typical wood adsorption and desorption isotherms and was consistent with the general wood behaviour. Equilibrium moisture content of pine WTNC was little increased at all relative humidities compared to the control during the hygroscopicity and evaporation. However, the response of beech WTNC to vapor was different, namely adsorption isotherm of beech WTNC and control was nearly same and desorption isotherm of beech WTNC went up more than control.

5.3.8 Biological resistances

5.3.8.1 Fungal decay

The results of pine and beech wood treated with different OMMT-based complexes were given in table 5-7, where the mass loss (%) is used as an inverse measure of the decay resistance. In this study, the virulence of fungal strains confirmed the validity of the test (mass loss of control samples above 20%).

The overall results of the studies indicated that success to prevent the brown rot on only pine wood treated with complexes of tannin-hexamine-boron and OMMT, and failure to resist the attacks of the *C. versicolor,* and *C. puteana* on other tested formulations.

Considering the results from table 5-7, notwithstanding the samples to be leached, it appeared that very low decay rates are obtained with the brown rots on pine WTNC samples. For beech

WTNC samples, the unleached samples were decay resistant. The samples leached according to the mild procedure ENV1250-2 present mass loss of 12.5%, proving that there is still a limited effect of the treatment. All the other leached samples (ENV1250-2 or EN84) present decay rates comparable to the control ones.

Table 5-7 Fungal resistance results of WINC samples exposed to two fungi in temperate climatic conditions

Sample		Leaching	Moisture content of WTNC at the end of the test (%)	Average mass loss of WTNC (%)	Moisture content of control samples at the end of the test (%)	Average mass loss of control samples (%)
Pine WTNC	Hexamine	No	86.16(9.79)	2.49(0.25)	76.95(7.09)	60.34(3.96)
		EN 84	52.17(8.21)	3.74(0.95)	81.83(10.15)	53.75(3.77)
		ENV 1250-2	37.98(6.66)	2.75(0.34)	71.28(16.45)	49.85(6.70)
	No hexamine	No	79.99(9.03)	2.41(1.57)	79.83(13.07)	62.48(3.71)
		EN 84	79.04(15.13)	42.56(7.80)	81.73(12.40)	48.14(9.53)
		ENV 1250-2	79.58(13.08)	36.03(9.36)	80.87(12.83)	41.36(11.46)
Pine treated with boric acid and OMMT		No	57.18(16.78)	0.49(0.30)	83.98(10.17)	62.14(4.12)
		EN 84	77.56(11.45)	64.54(2.79)	84.27(7.64)	66.00(1.54)
		ENV 1250-2	88.37(4.52)	64.82(1.49)	88.93(4.78)	62.26(7.47)
Beech WTNC	Hexamine	No	82.72(13.49)	2.51(0.56)	78.54(13.15)	46.91(14.56)
		EN 84	76.84(12.98)	31.98(5.67)	83.79(7.98)	53.28(14.23)
		ENV 1250-2	83.24(15.59)	12.46(3.13)	79.98(12.45)	52.69(14.60)
	No hexamine	No	84.08(14.11)	2.27(1.66)	78.89(18.97)	48.41(4.37)
		EN 84	79.84(15.93)	51.66(6.79)	87.11(8.78)	52.26(9.95)
		ENV 1250-2	80.49(8.99)	52.97(7.10)	79.98(18.96)	56.87(11.41)
Beech treated with boric acid and OMMT		No	60.79(21.28)	0.95(0.38)	79.93(19.09)	49.85(7.86)
		EN 84	67.05(20.99)	42.10(10.82)	78.93(18.88)	44.59(6.39)
		ENV 1250-2	78.93(7.99)	41.08(8.17)	84.57(10.23)	50.06(11.76)

Note: Standard deviations are given in the parenthesis.

5.3.8.2 Termite deterioration

The results of termite screening test are given in table 5-8.

This screening test is valid as the pine sapwood and beech controls present a strong attack (visual rating 4) and above 50% of the termite workers remain alive at the end of the test.

In the test devices containing the treated specimens without leaching, all the termites died (mortality 100% after 2 weeks of exposure) but they had been chewed at the edge. After termite activities had disappeared, a large number of molds and mold spores overspread some samples.

Table 5-8 Resistance of treated wood against termites

Sample		Leaching	Survival of termite		Level of specimen damaged (%)					Weight loss (%)
			Workers (%)	Soldiers (S) and /or nymphs (N)	0	1	2	3	4	
Pine WTNC	Hexamine	No	0	0	0	16.7	83.3	0	0	4.54 (0.12)
		EN 84	47.20 (6.10)	S. N.	0	0	0	0	100	4.01 (1.34)
		ENV 1250-2	0	0	0	0	0	0	100	3.32 (0.23)
	No hexamine	No	0	0	0	100	0	0	0	3.29 (0.97)
		EN 84	61.60 (3.85)	S. N.	0	0	0	0	100	5.33 (0.77)
		ENV 1250-2	44.80 (6.10)	S. N.	0	0	0	0	100	4.30 (1.51)
Pine treated with boric acid and OMMT		No	0	0	0	100	0	0	0	1.21 (0.29)
		EN 84	70.81 (8.67)	S. N.	0	0	0	0	100	20.59 (1.11)
		ENV 1250-2	66.43 (12.28)	S. N.	0	0	0	0	100	18.29 (2.13)
Beech WTNC	Hexamine	No	0	0	0	50.0	50.0	0	0	2.81 (1.07)
		EN 84	26.21 (8.01)	S. N.	0	0	100	0	0	2.33 (1.17)
		ENV 1250-2	0	0	0	50.0	50.0	0	0	3.75 (1.56)
	No hexamine	No	0	0	83.3	16.7	0	0	0	3.90 (0.79)
		EN 84	53.61 (4.56)	S. N.	0	0	0	0	100	8.74 (1.24)
		ENV 1250-2	54.00 (4.90)	S. N.	0	0	0	16.7	83.3	6.48 (1.45)
Beech treated with boric acid and OMMT		No	0	0	100	0	0	0	0	2.44 (1.83)
		EN 84	51.20 (7.82)	S. N.	0	0	0	0	100	9.96 (1.08)
		ENV 1250-2	62.00 (4.00)	S. N.	0	0	0	0	100	9.90 (0.51)
Pine control		No	75.33 (10.32)	S. N.	0	0	0	0	100	18.98 (1.45)
Beech control		No	68.67 (7.66)	S. N.	0	0	0	0	100	10.74 (1.71)

Note: Standard deviations are given in the parenthesis.

Table 5-8 stated that termites had ingested less pine and beech WTNC with hexamine resin than others and severely attacked other formulations. The visual ratings of treated specimens

without leaching were only slightly attack (visual rating 0 or 1) excluding the formulation containing hexamine. These statements were done with the visual rating, which cannot be done with the weight loss.

5.3.9 Fireproofing properties

5.3.9.1 Analysis by the simplified lab-scale apparatuses

The simplified lab-scale tests were conducted to gain a comparative analysis of fire resistant properties. Two types of simulation tests were considered: short- and long-time exposure tests. Ignition, flame and ember time represented a good evaluation of the ignition process, which were obtained by the short-time exposure tests (Table 5-9).

The fire-retardant effect of WTNC was also evident for these nanocomposites: increasing of the ignition time and decreasing of the flame and ember times compared with the controls.

Table 5-9 Short-exposure fire tests for WTNC

Wood species	Treatment	Ignition time (s)	Flame time (s)	Ember time (min)
Pine	Nano-modification	16.33	42.67	2.50
	Control	8.60	192.00	4.90
Beech	Nano-modification	20.67	62.00	2.44
	Control	12.40	293.00	8.99

Longer-fire exposure proved the presence of complexes of tannin-hexamine-boron resin and OMMT in the preservative to reach a sensible fire-proofing degree. The weight loss for wood samples is shown in figure 5-26.

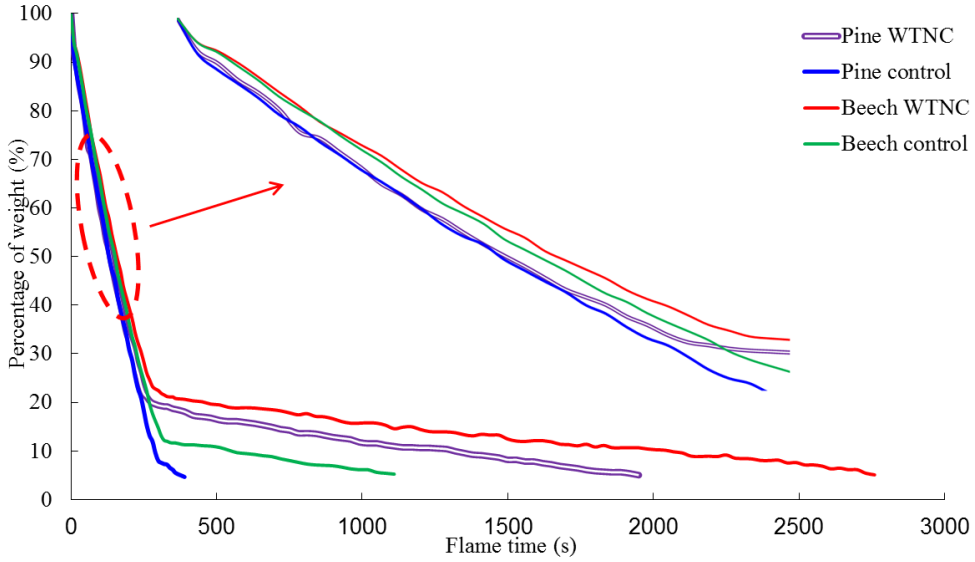


Figure 5-26 Weight loss of WTNC samples on long-fire exposure tested apparatus

The constant monitoring of these long-term exposure tests produces curves with the same tendency. From the start up to 80% weight loss, the difference between treated and control samples are barely noticeable. In the case of impregnating complexes of tannin-hexamine-boron resin and OMMT, the slope of curve for pine WTNC was nearly same prior to that of

the relative control sample; but that of beech WTNC was slightly mitigatory with comparison to one of the relative control sample.

After 80% weight loss of the samples, the flame time is always longer for the treated samples. Furthermore, even if this shift happened when the weight loss was already substantial (around 80%), it still allows the sample to resist the burning process for at least twice the time required to complete the burning.

5.3.9.2 Analysis by cone calorimeter

This section contained the data and analysis for combustion conducted by cone calorimetric. With comparison to the investigations simplified by the lab-scale equipment, this apparatus would export much more parameters of combustion. These properties determined the rate at which heat was released from wood when it burnt, the smoke production and the toxicity of the gases. Other important parameters that helped the understanding of the combustion related to wood were emission of toxic gases and mass loss rate.

Table 5-10 Data recorded in cone calorimeter experiments at a heat flux of 50kW/m^2

Samples	PHRR (kW/m^2)	THR (MJ/m^2)	TSR_{whole} (m^2/m^2)	SEA_{peak} (m^2/kg)	TTI (s)	TTF (s)	CO_{peak} (kg/kg)	$CO_{2,peak}$ (kg/kg)
Pine WTNC	366.8	61.6	239.2	230.1	34	410	0.3612	4.79
Tannin-treated pine	493.5	68.9	355.3	345.2	26	384	0.2608	4.69
Pine control	321.1	60.1	366.4	381.7	22	424	0.5801	9.95
Beech WTNC	517.2	75.3	247.7	149.2	36	460	0.1819	3.37
Tannin-treated beech	635.4	78.1	221.4	134.5	34	452	0.1952	7.62
Beech control	717.3	82.5	167.8	113.0	31	444	0.9607	10.35

The fire behavior data of WTNC and other treated wood were summarized in Table 5-10. The peak heat release rate (PHRR) and total heat release of beech WTNC was lowest among all testing formulations. However, these improvements were not shown with pine WTNC. The addition of complexes of tannin-hexamine-boron and OMMT had effectively increased the time to ignition (TTI) and time to flame out (TTF) of beech WTNC in contrast to only tannin-hexamine-boron formulation. For pine WTNC, TTI had been prolonged by the nanoclay and tannin resin, which could not be increased TTF. In general, the suppressed second peaks of HRR curves and the prolonged flameout time provided further evidences for the effective barrier. The evolution of carbon monoxide and smoke indicated some complicated varieties when discussed between modified wood and control.

Average heat release rate (HRR) during WTNC combustion was arranged figure 5-27, which was computed over a fixed 5~10 min period. The HRR curve indicated that treated pine WTNC presented better combustion behaviour than control, but beech wood conducted the treatment decreased HRR than control. In the cone calorimeter measurement of wood at the

beginning of burning showed a sharp peak. As the burning proceeds and a char layer were formed on the surface of wood, the HRR value decreases. The increasing uptake of tannin and OMMT had an influence on lowering the first HRR. Both the middle range of the HRR curve as well as the second peak decreased in intensity with increasing tannin and OMMT in beech wood. However, the middle HRR figure of pine WTNC was placed below that of control and was nearly same trend with that of tannin-treated wood; as unexpected, especially the second peaks HRR of treated pine wood were higher than control. These results suggested that the treated formulations as improving flame retardant had an effect to beech wood only.

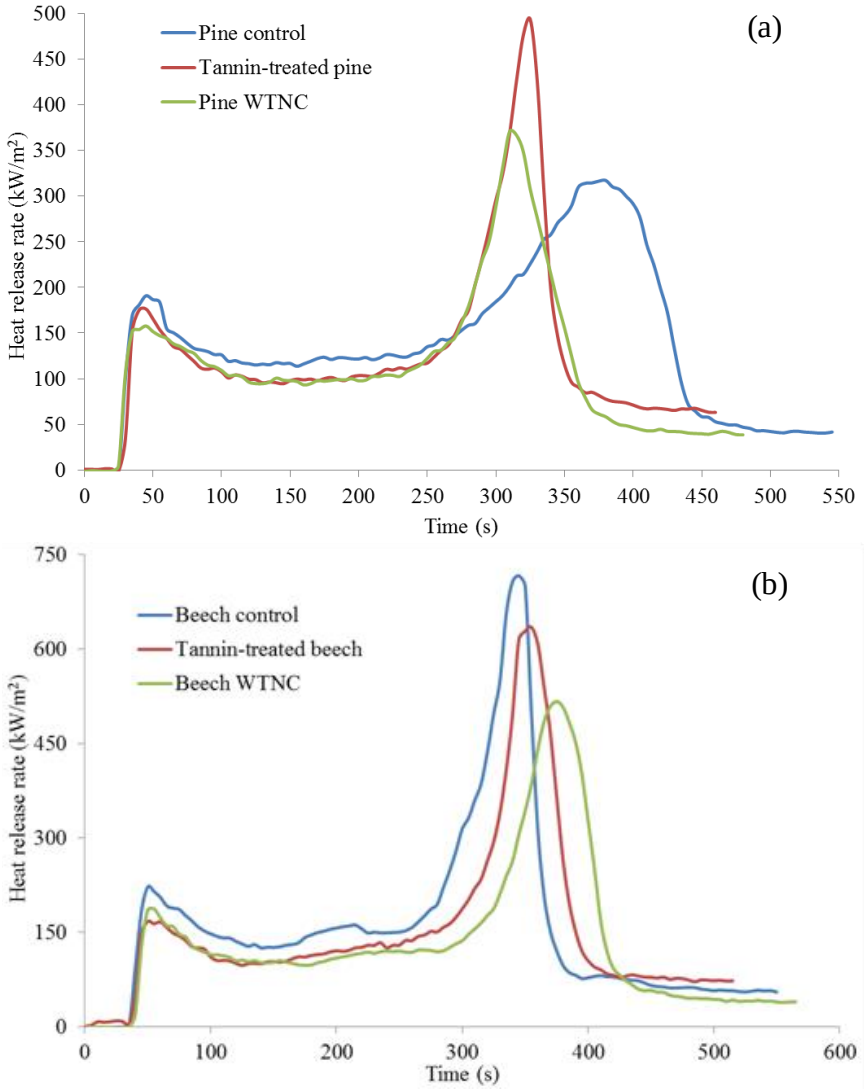


Figure 5-27 Heat release rate history of pine (a) and beech (b) WTNC at an external heat flux of 50kW/m^2

In Figure 5-28 there are the total smoke release (TSR) curves, showing the same two-step trend on the beech material as was observed on the pine samples. The effect was observed on pine samples, impregnated with tannin-hexamine-boron solution, followed by pine specimen impregnated with the complexes of tannin resin and OMMT. As unexpected, the TSR figure was complex for beech samples: impregnated samples in first steps showed low smoke release than controls, with a slightly bigger second step of TSR than control samples, namely much more smoke produced in second step. Furthermore, the first step of tannin-hexamine-boron-

treated and nano-modified wood was crossed. This parameter also confirmed the two steps of smoke formation, the curves of treated samples were close.

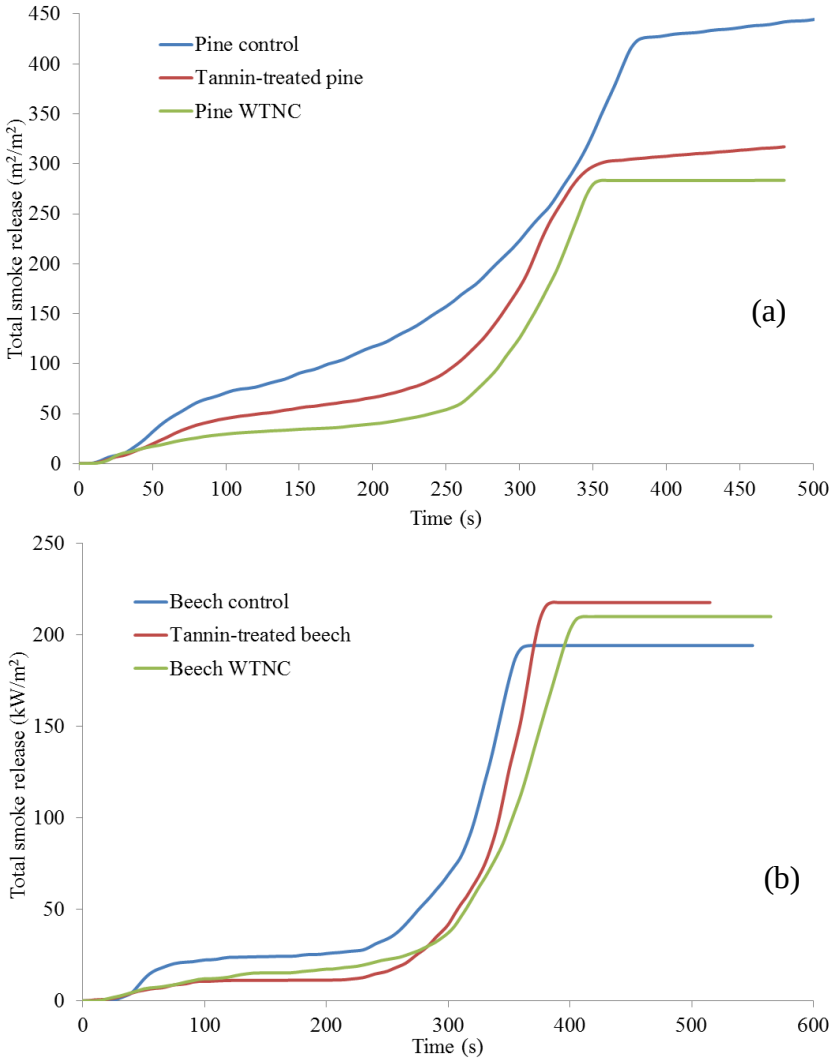
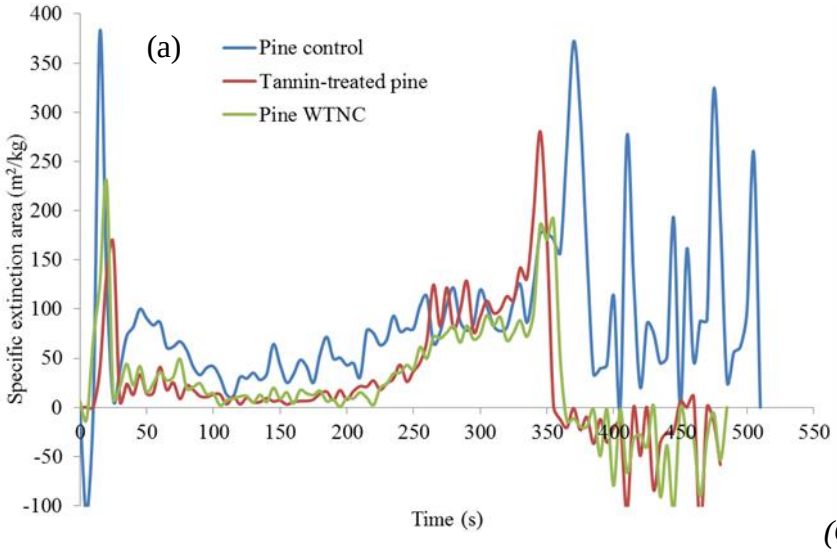


Figure 5-28 Total smoke release of pine (a) and beech (b) WTNC at an external heat flux of 50kW/m^2

The specific extinction area (SEA) of smoke as combustion time was presented in figure 5-29 and the smoke production rate of smoke as the function of time was shown in figure 5-30. For



(Continued)

Figure 5-29 *(Concluded)*

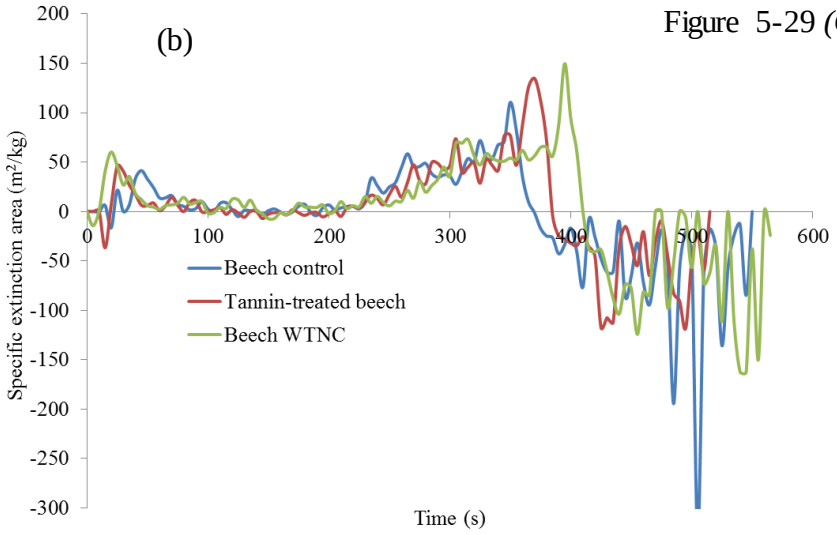


Figure 5-29 Specific extinction area of pine (a) and beech (b) WTNC at an external heat flux of 50kW/m^2

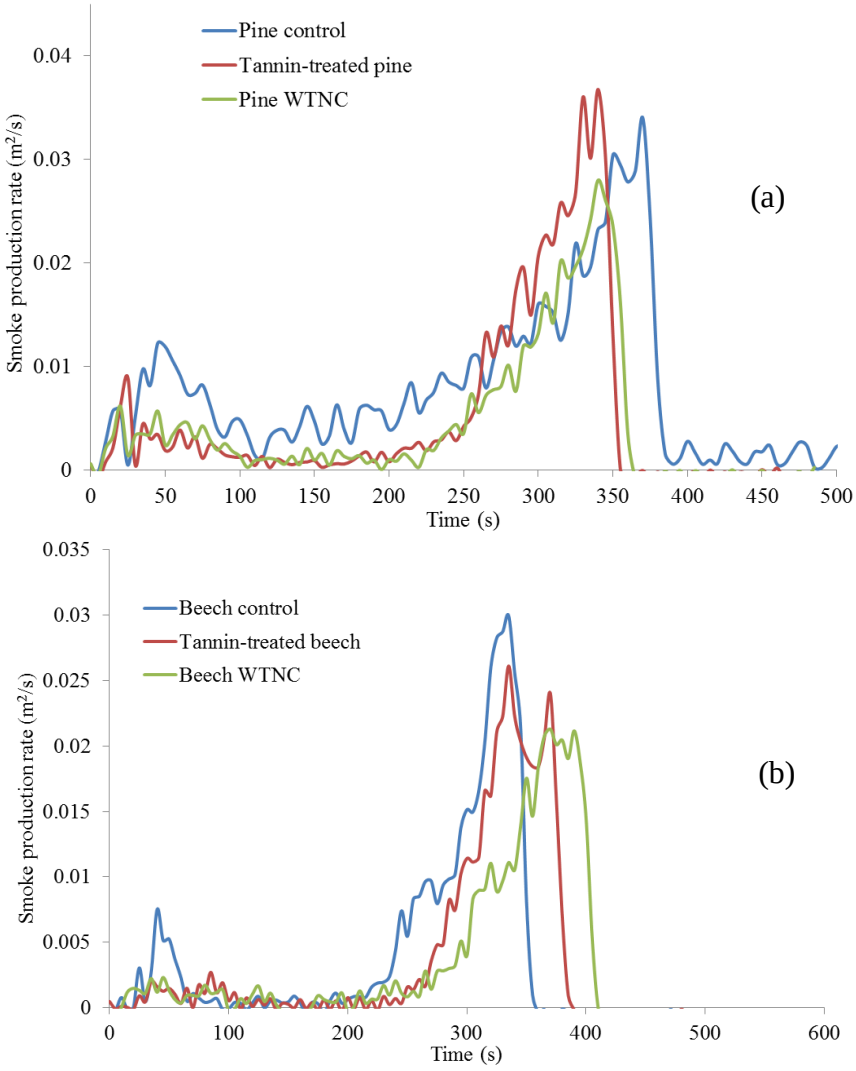


Figure 5-30 Smoke production rates of pine (a) and beech (b) WTNC at an external heat flux of 50kW/m^2

untreated control smoke was formed mostly at the beginning of burning and shortly prior to the end of burning. The effect of multifunctional additives as the flame suppressant was

obvious for pine wood and ambiguous for beech wood. But at the end of combustion, for all beech wood SEAs were inspected the negatives, furthermore, the smoke production rate (SPR) was also diminished. The SEA and SPR of pine control was the highest among the selected pine samples, but after the highest heat release SEA and SPA of tannin-treated wood achieved a biggest. During the flowing, SEA and SPA of all samples against changed to the different shape in contrast to the previous pattern. All in all, for all treated wood, the second peak of smoke formation was eliminated.

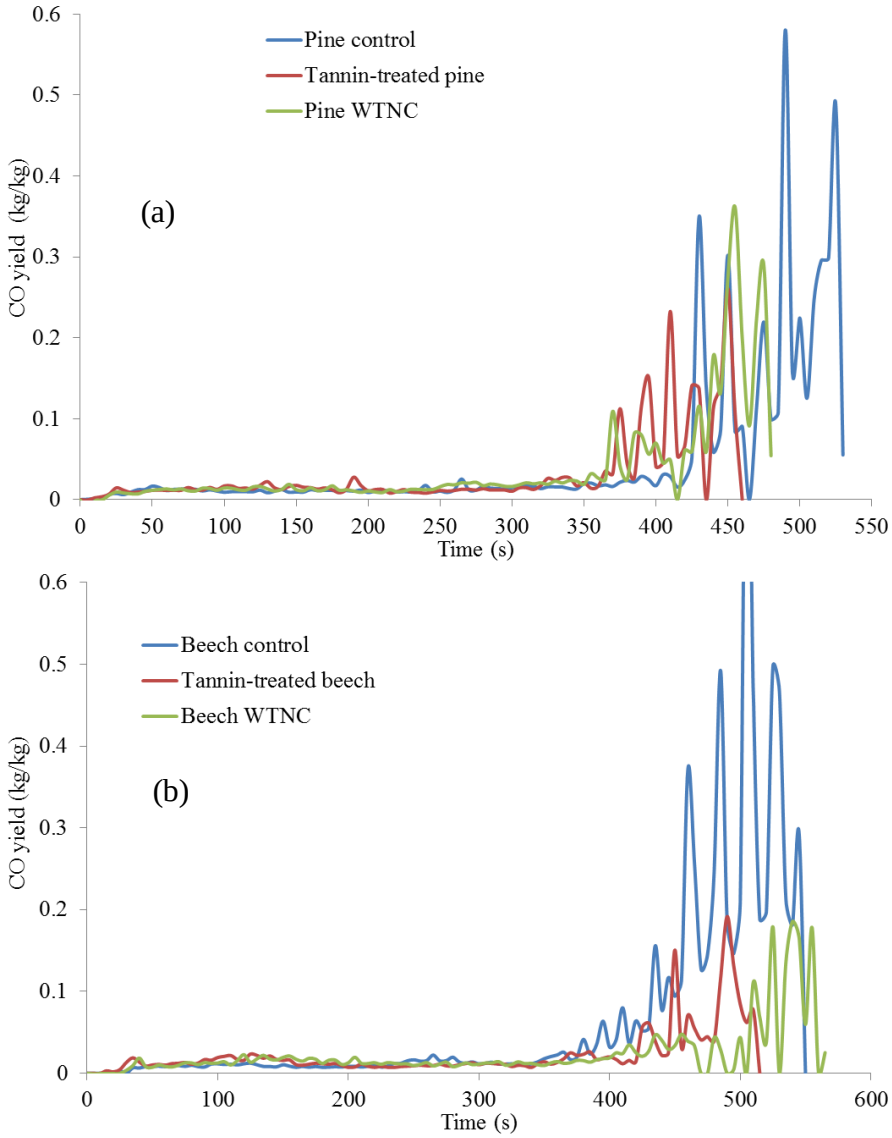


Figure 5-31 CO yield of pine (left) and beech (right) WTNC at an external heat flux of 50kW/m^2

Yields of CO and CO_2 depended on the material burning and the ventilation conditions. Figure 5-31 and 5-32 respectively presented the CO and CO_2 production versus time evolved in the cone calorimeter. The curve trend of CO generated by all wood samples was different to discriminate. Notwithstanding it was interesting to note that the production of CO from tannin-treated beech and beech WTNC decreased at the end of combustion. The treated pine and beech wood produced slightly low CO_2 amounts in comparison with pine and beech controls.

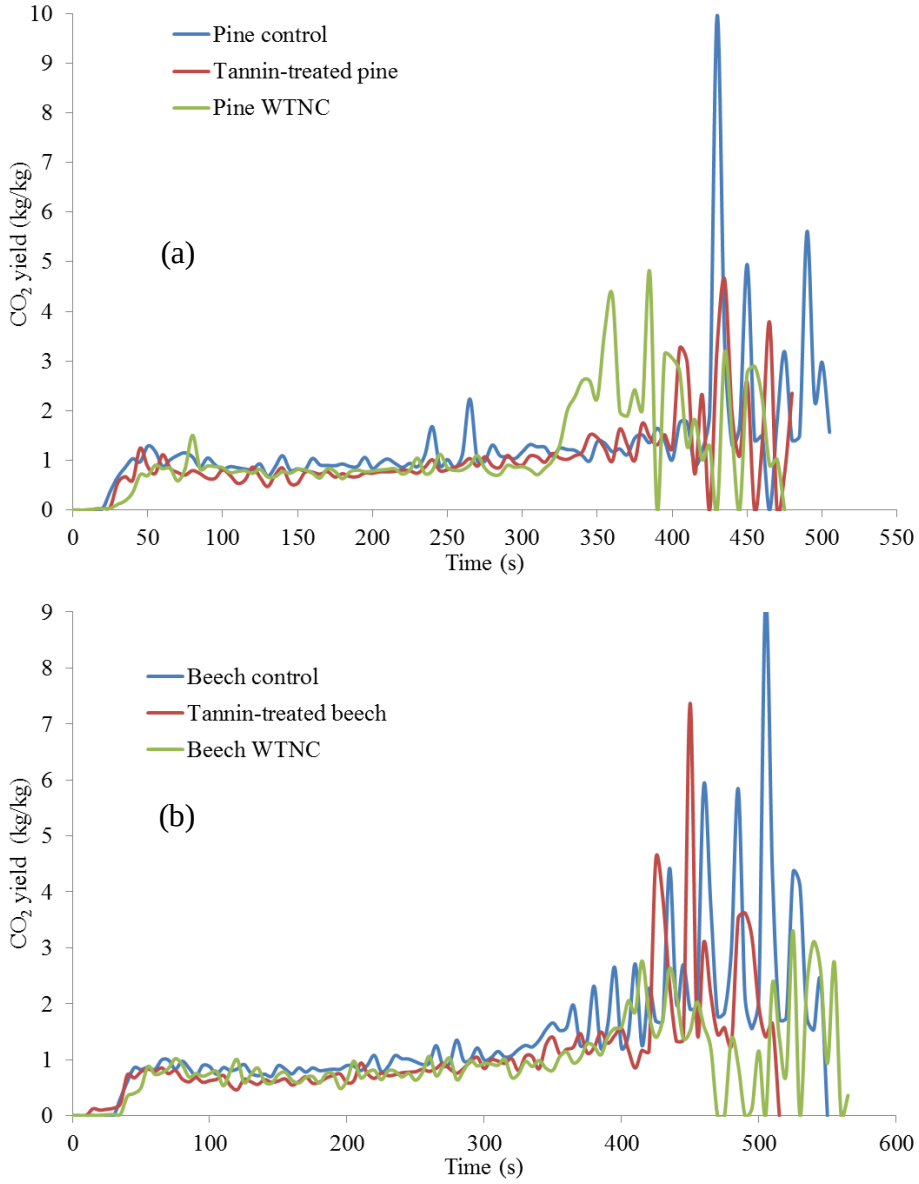
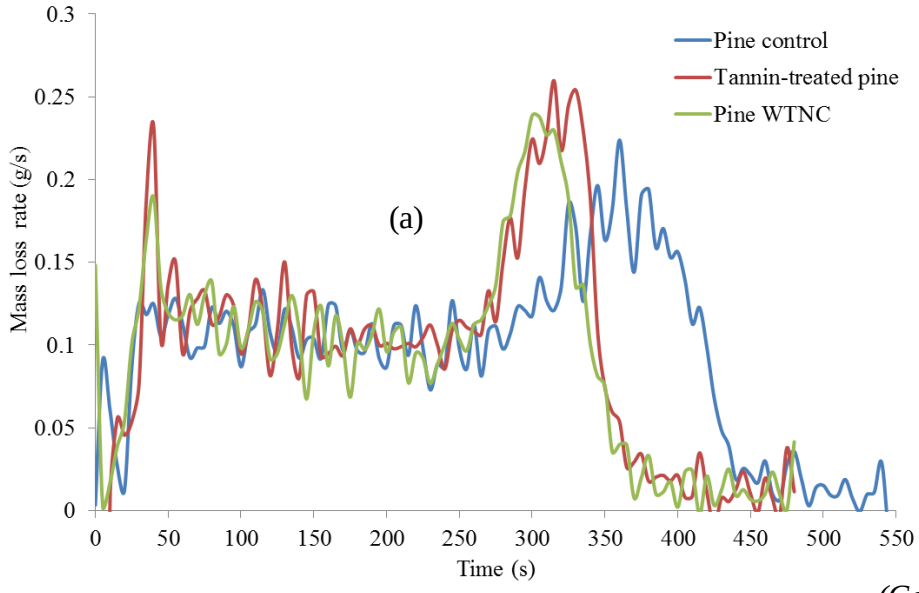


Figure 5-32 CO_2 yield of pine (a) and beech (b) WTNC at an external heat flux of 50kW/m^2



(Continued)

Figure 5-33 *(Concluded)*

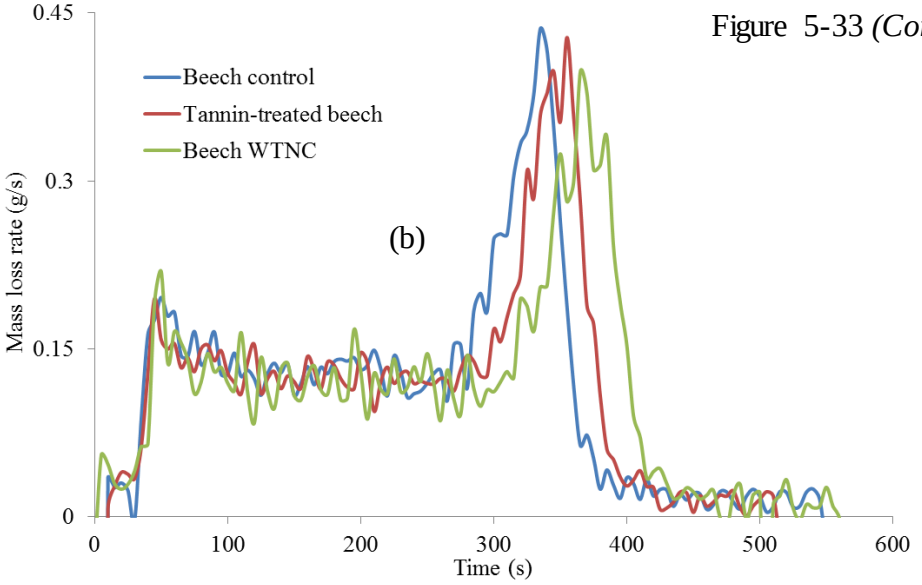


Figure 5-33 Mass loss rates of pine (a) and beech (b) WTNC at an external heat flux of 50kW/m^2

Examples of the mass loss rate (MLR) curves were illustrated in figure 5-33. The mass loss rate results from pyrolysis, which is controlled by the net heat flux, the decomposition temperatures, heat transfer and kinetics. Therefore, the shape of MLR curves for all tested wood was nearly similar with that of HRR figures. During the combustion of wood sample, slower HRR was, less MLR was. Before the presence of second peak of MLR, the curves of wood sample performed in this study nearly overlapped.

5.3.10 Evaluation of thermal degradation

5.3.10.1 Thermogravimetric analysis

Figure 5-34 presented the thermal stabilities of original MMT, OMMT and complexes of tannin-hexamine-boron and OMMT, which illustrated degradation steps in the temperature range of 100–600 ℃. The weight loss in the MMT's TGA curve near 100 ℃ may be ascribed

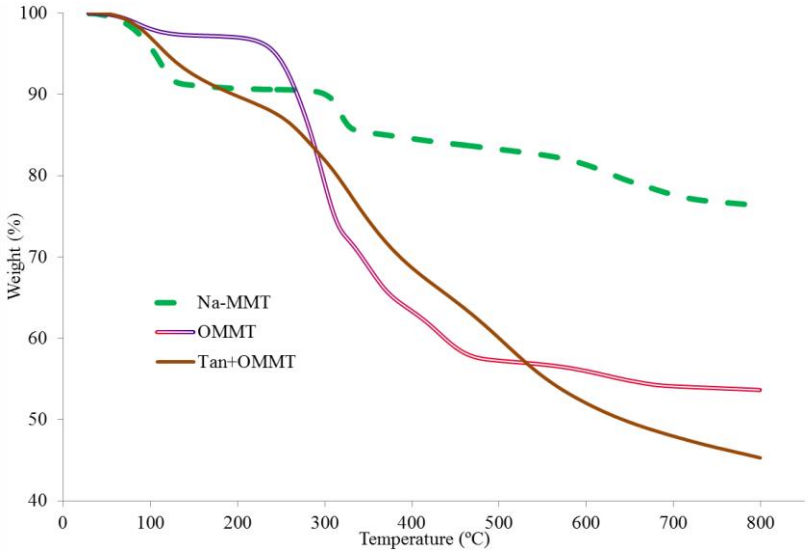


Figure 5-34 TGA thermograms of MMT, OMMT and complexes of tannin-hexamine-boron resin and OMMT

to interlayer water associated with the exchangeable Na^+ ions with a minor contribution from free water held in interparticle pores. The weight loss in the MMT's TGA curve near 320 ℃ was associated with the loss of structural water through dehydroxylation of the montmorillonite layers (Hedley et al. 2007). For OMMT, the evolution of absorbed water and gaseous species was estimated from the mass loss between 50 and 100 ℃. The weight loss for the OMMT from 200 ℃ could sustain longer than for MMT. The results in figure 5-34 showed that an increase of weight loss in OMMT compared to complexes of tannin-hexamine-boron resin and OMMT at the decomposition temperature range (around 530 ℃). However, the mass loss was slowed down in complexes of tannin-hexamine-boron resin and OMMT compared to OMMT between 280 and 530 ℃.

Table 5-11 Results of thermogravimetric analysis

Sample	Total weight loss at 800 ℃ (%)	Temperature of rapid pyrolysis (℃)
Pine WTNC	77.51	370
Pine control	85.51	365
Beech WTNC	79.34	361
Beech control	85.03	357

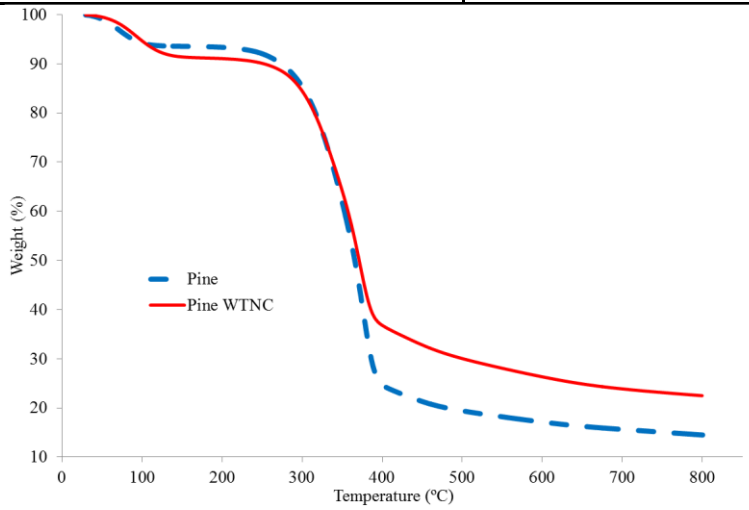


Figure 5-35 TGA curves of pine BTNC and control

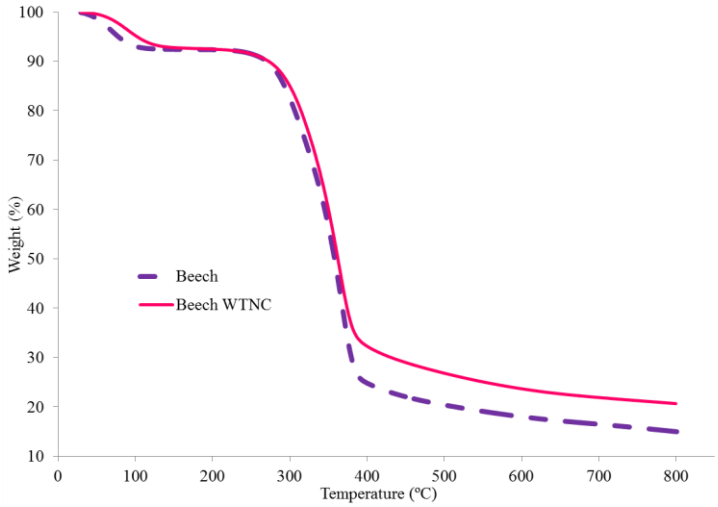


Figure 5-36 TGA curves of beech BTNC and control

As seen in table 5-11, complexes of tannin-hexamine-boron resin and OMMT had a fire retarding effect. The treatment with tannin-boron-hexamine-OMMT complexes lowered the total weight loss from 88.51% to 77.51% (compared to control) for pine wood and from 85.03% to 79.34% for beech wood. Also temperature of rapid pyrolysis was lowered. For both wood species in the case of nanoclay-treated impregnation, the decomposition temperatures were increased, moreover, the TGA curves shifted to higher temperature (Figure 5-35 and 5-36).

5.3.10.2 Thermal differential simultaneous analysis (simultaneous DSC-TGA)

Figure 5-37 and 5-38 separately showed the TGA, DTG and DSC of MMT and OMMT analyzed by simultaneous DSC - TGA. From 25℃ to 200℃, the DTG peak and corresponding exothermic peak in the DSC curve were dominated by the volatilization of absorbed water for MMT and OMMT. Following the region between 200 and 500℃, the DTG peak and DSC endothermic peak mainly involved some oxydation reactions in OMMT. Namely three overlapping peaks of DTG and DSC for OMMT indicated that the release of

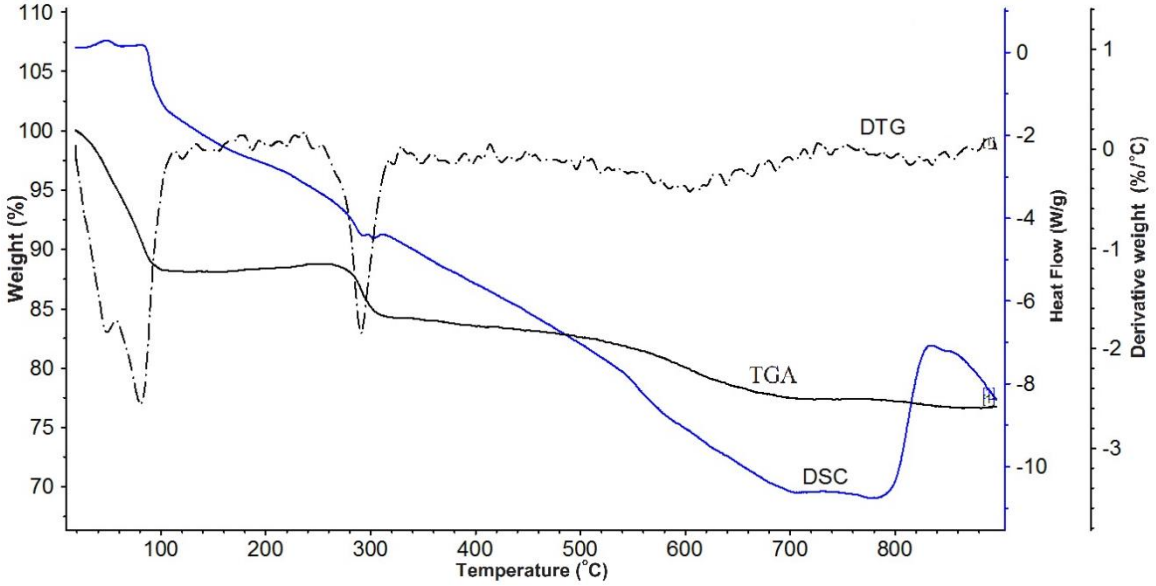


Figure 5-37 Simultaneous DSC - TGA curves (TGA, DTG and DSC) of MMT

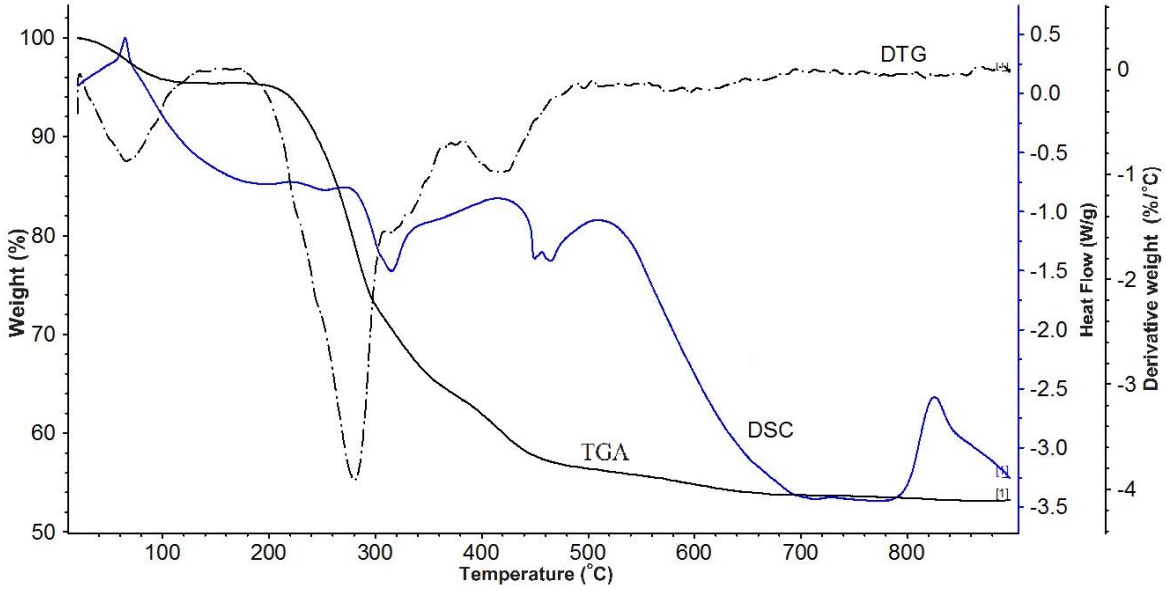


Figure 5-38 Simultaneous DSC - TGA curves (TGA, DTG and DSC) of OMMT

organic substances was staged, arising from different mechanisms. But MMT showed no reaction in this region. Peaks between 500 and 800 ℃ for MMT and OMMT were conveniently related to the dehydroxylation of the silicate structure (Hedley et al. 2007, Huskić et al. 2008). The region over 800 ℃ where organic carbon reacted in some yet unknown way could not be elaborated. The free water content from the TGA curves was about 13% and 5% for MMT and OMMT, respectively.

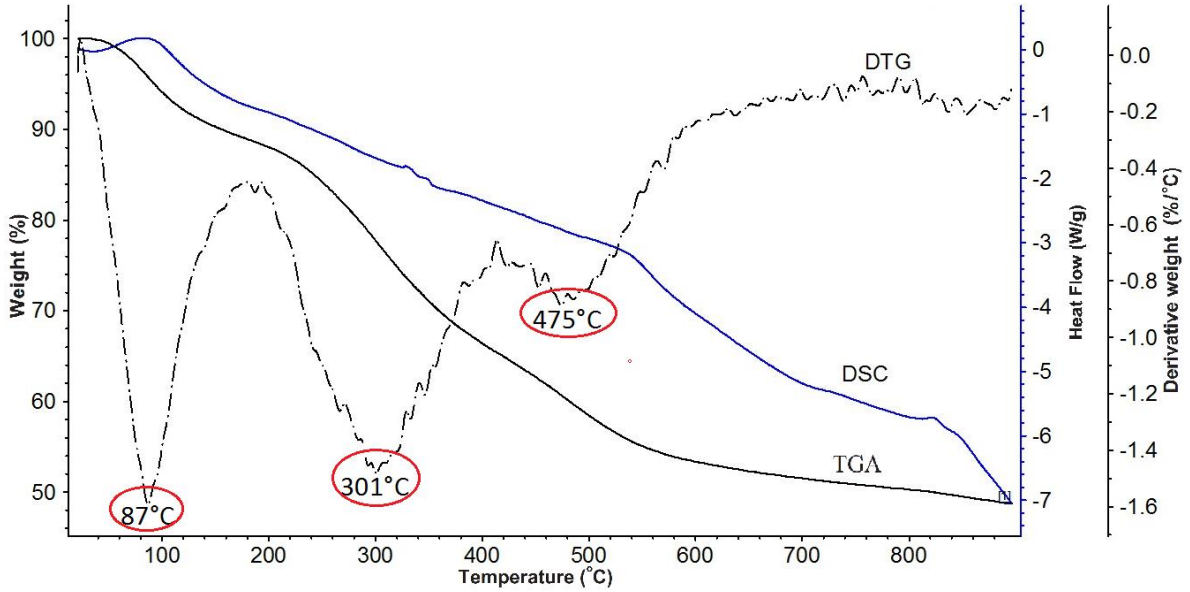


Figure 5-39 Simultaneous DSC - TGA curves (TGA, DTG and DSC) of complexes of tannin-hexamine resin and OMMT

Figure 5-39 showed the TGA, DTG, and DSC curves from 20 to 900 ℃ for the complexes of tannin-hexamine-boron resin and OMMT. The nanocomposites revealed three-stage degradation: the first stage attributed to the volatilization of the water content from the sample, while the second and third stage corresponded to the thermal cracking of the carbonaceous conjugated polyene sequences. The three peaks in the derivative thermograms give indications of the maximum weight loss rate of the degradation corresponding to the quickest degradation temperature of each stage.

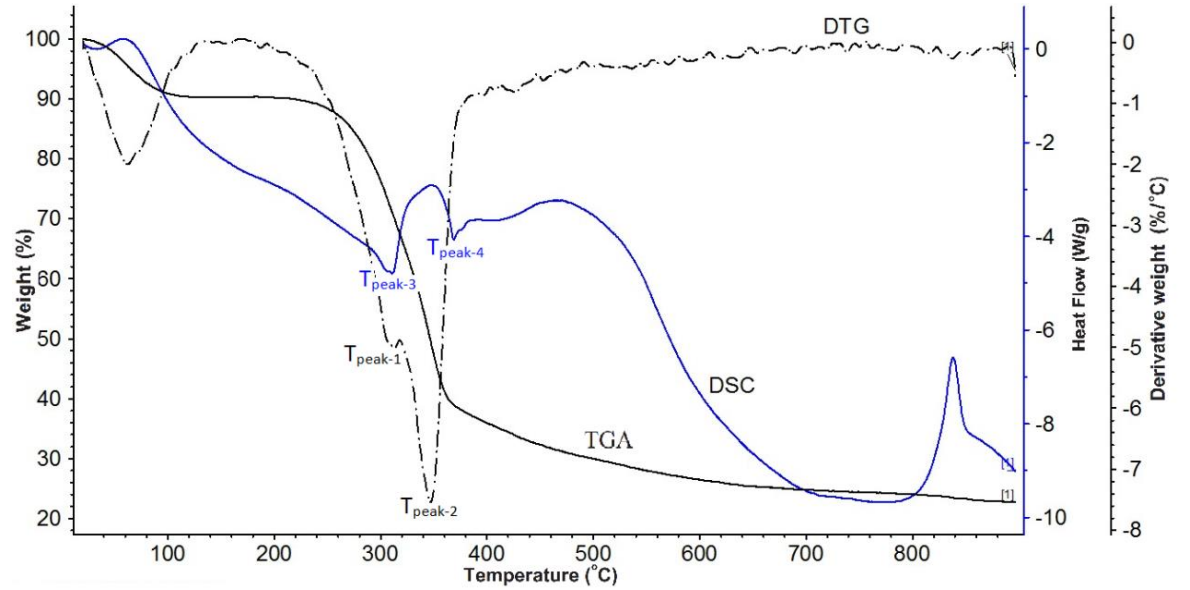


Figure 5-40 Simultaneous DSC - TGA curves (TGA, DTG and DSC) of pine WTNC

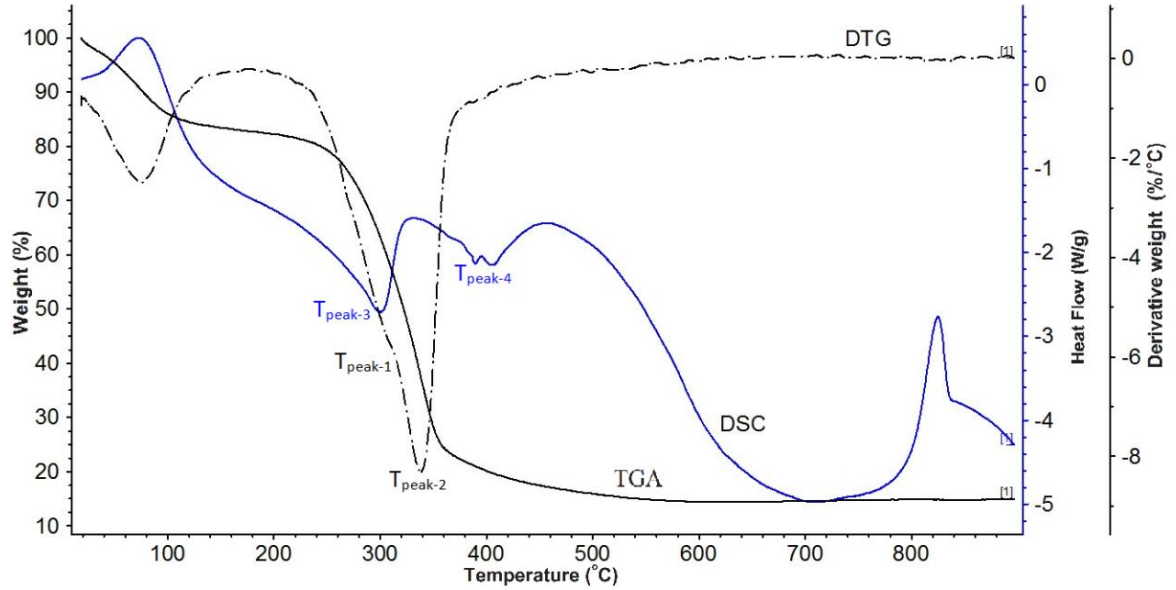


Figure 5-41 Simultaneous DSC - TGA curves (TGA, DTG and DSC) of beech WTNC

Analyzing simultaneous DSC - TGA curves of pine and beech (Figure 5-40 and 5-41), it was verified that the result of TGA, DTG and DSC between them was close, excluding the small shoulder of DTG curve and slight shift of second endothermic peak from beech WTNC. The representative DTG curve of wood revealed two decomposition regimes: the peak at higher temperatures is mainly due to the decomposition of the cellulose and the shoulder, at lower temperatures, can be attributed to the decomposition of the hemicellulose. A peak due to the lignin degradation cannot be observed. In fact, the differences in wood species were mainly due to the different thermochemical behavior of lignin degradation and that of the first step of the hemicellulose degradation (Müller-Hagedorn et al. 2003).

Table 5-12 Thermal data obtained by simultaneous TGA－DSC

Sample	TGA				DSC	
	T_{peak-1} (℃)	T_{peak-2} (℃)	H_2O (wt%)	Residue (wt%)	T_{peak-3} (℃)	T_{peak-4} (℃)
Pine WTNC	313	347	4.44	22.71	311	369
Beech WTNC	296	337	9.74	14.90	299	405
Pine control	300	335	5.89	19.37	298	340
Beech control	283	326	11.57	10.15	284	327

It can be observed from table 5-12 that the thermal decomposition temperatures of two wood species were close, no matter the treatment. As determined by the curve of DSC, the thermal decomposition peak values ($T_{peak3\ and\ 4}$) were very similar to those obtained from the DTG degradation curve at the maximum mass loss peak temperature ($T_{peak1\ and\ 2}$). The simultaneous DSC - TGA technique showed that DTG and DSC curves presented a unique decomposition endothermic event at higher temperature which can be influenced by the nanoclay.

5.4 Discussions

The layer silicates used most commonly (montmorillonite, hectorite, saponite, etc.) in the preparation of polymer/layer silicate nanocomposites, were widely used as filler for rubber and plastic for many years, for saving polymer consumption and reducing the cost (Mehrotra and Giannelis, 1989; Vaia et al. 1995, Wang and Pinnavaia 1998, LeBaron et al. 1999, Mittal 2009). Clay minerals were hydrophilic and only miscible with hydrophilic polymers. Hence, modifying the clay mineral surface with cationic surfactants (for example quaternary alkyl ammonium ions), to convert the normally hydrophilic silicate surface to an organophilic surface, was a strategic step for the preparation of polymer/layer silicate nanocomposites. These entering molecules can either simply increase the distances between the still-parallel layers in an intercalation process or randomly entirely disperse the separate layers in an exfoliation. In wood modification, clay layers impregnated via tannin-hexamine-boron resin and dispersed at a nano scale in solid wood acted as a reinforcing phase to form an important class, called wood polymer nanocomposites, which exhibited substantial improvement in wood properties in terms of dimensional stability, water repellency surface, hardness, modulus of elasticity, flame retardant, etc (Xue and Zhao 2008, Cai et al. 2008, Yu et al. 2011, Hazarika and Maji 2013).

In this study, the structure of clay-based nanocomposites had been characterized extensively using techniques such as FTIR, XRD. The morphology of nanoclay and tannin resin was depicted by microscopy and SEM. Experimental results of physical and mechanical properties for WTNC such as water absorption, water repellence, dimensional stability, surface hardness, axial compression, bonding strength, bio-susceptibility and flame retardant were also obtained and indicated partially debatable, even though only 3% nanofillers and 10% tannin-hexamine-boron were added.

Firstly, FTIR is a useful way to investigate the characteristics of clays and the related materials. The preparation of the modification-MMT was based on a cation-exchange reaction with CTAB. The frequencies of the asymmetric and symmetric $–CH_2$ stretching absorption bands were sensitive to the conformation of the intercalated surfactants within the clay interlayer space. The appearance of this band may be taken as the sign of successful organmodification. The change of the clay surface affinity (hydrophobic and hydrophilic) was indicated by the frequency shifts and intensity of hydroxyl stretching and bending vibrations of the absorbed water. The Si–O–Si group belonged to MMT, which corresponded to well-ordered montmorillonite, can be inspected in the spectra of WTNC, no matter how pine and beech. The result proved: the modification of the hydrophilic Na-MMT surface layers to become hydrophobic was the initial stage to disperse MMT uniformly into wood matrix via tannin resin. As a result of this surface modification, the surface of the MMT would have a hydrophobic and organophilic characteristic. Thus, there would be hydrophobic environment in the MMT gallery surfaces to accommodate the hydrophobic tannin resin due to the compatibility between them. In other words, the polarity of the organoclay sufficiently matched tannin prepolymer, it will intercalate into the galleries, furthermore spreading clay layers apart.

The silicate-interlayer spacing and the crystallinity of WTNC were calculated from the XRD measurements, which gave the values of the basal distance between silicate layers and

crystallite size in wood. It is clearly shown that the interlayer spacing increased with the increase of the size of surfactant: from 1.56 nm for Na-MMT to 3.29 for OMMT. The XRD pattern of complexes of tannin resin and OMMT also demonstrated that the MMT intercalated surfactants was compatible with tannin-hexamine-boron resin. However, the dimensions of the crystal lattice for pine and beech WTNC did not evidently change after impregnating complexes of tannin-hexamine-boron resin and OMMT from the XRD spectra. Notwithstanding the diffraction patterns of mechanical mixture for wood powder, tannin-hexamine-boron resin and OMMT presented clearly some peaks of OMMT. Comprehensively, although nanoclay increased, wood maintained its original crystalline structure from only the result of XRD spectra. But it was possible that the interlayer of MMT was exfoliated. All these suggested that the crystallinity degree of wood in WTNC decreased, MMT exfoliated and some silicate nanolayer were inserted into the amorphous region of cellulose of wood cell walls.

Morphological photographs could establish the microstructure of the material. TLM and SEM pictures respectively described the structure of different levels for wood cells. With regard to Scots pine, the longitudinal penetration of solution through tracheids was easier for latewood because its bordered pits are rarely closed (Bamber and Burley *1983*; Liese and Bauch *1967*), while the bordered pits of earlywood were often closed and only wet conditioning of the samples or strong vacuum-pressure cycles could allow passing of the liquid through these pits. Furthermore, when tannin-hexamine-boron solutions mixed OMMT were applied, there was a decrease in the capillary effect (especially for latewood tracheids) which resulted in the lower impregnation rate. The penetration of ray parenchyma cells was not limited because their average thickness of around 150–200 μm allowed the passage of tannin-hexamine-boron solution. In terms of hardwood, the porous structure possessing the larger vessels ensured an easy and deep impregnation by tannin-OMMT solutions. Anyway, the majority of the penetration was longitudinal and if this penetration was weak the impregnated effect was a poor.

From microscopy results, the tannin solution penetrated into the cell and was stored in the lumen. Indeed, the molecules of these oligomers were too large to establish chemical bonding with the hemicelluloses of the cell walls. Possible interactions could be assumed with the interface lignin molecules because several studies of polymerization between tannin and lignin have been performed (Lei et al. 2008, Mansouri et al. 2010, Tondi et al. 2013), but no significant scientific evidence had been published to date.

SEM photography also indicated the attachment and insertion of the OMMT layer to the cell wall. In wood, the macropores, pores, nanopores, and other multilevel pore structures could accommodate OMMT intercalated and infiltrated on wood cells. The exfoliated intercalation of OMMT layers had a large radius/thickness ratio, thus pores and nanopores of wood were highly selective and properly orientational by intercalated and combined OMMT. There would be different combinations during OMMT intercalation, which ultimately led to multiple forms in wood composite, such as insert, exfoliation and granules. Furthermore, the bond among the fibers could be improved by tannin-hexamine-boron resin.

Since retention, as calculated from the uptake and concentration of the treatment solution, did not consider the selective absorption or uneven distribution of active ingredients, it did not seem to be very accurate for precisely determining the amount of biocide within the treated

wood (considering possible boron diffusion). However, the retention could influence wood properties, i.e. physics, mechanics, biological resistance (retention of active ingredients). In current study, when these residual unreacted complexes continually gathered, the primary vessel passages in beech wood were easily bulked and resulted in a lower retention with comparison to Scots pine (more paths). From the microscopic images, complex solution permeated into Scots pine sapwood by more paths than beech wood. Additionally, the XRD effects had proved that tannin-hexamine-boron resin had a better compatibility than tannin-boron resin without hexamine. So and OMMT could easily be introduced into wood by tannin-hexamine-boron resin.

It was apparent that the penetration of the complexes of tannin resins and OMMT in the wood cells reinforced the axial compression strength of the pine and beech WTNC, because the linear relationship between density and axial compression strength had been investigated (Timell 1986). Especially, the penetration in pine was incomplete and the distribution of the resin was not homogeneous, but the mechanical resistance was still increased.

The surface properties of the treated wood (only complexes of tannin-hexamine-boron resin and OMMT) were tested in order to evaluate their hardness and gluing capacities. Harder surfaces were achieved when wood were homogeneously filled with complexes of tannin-hexamine-boron resin and OMMT. The distortion of individual wood fibres was the starting point for the failure under compression (Kollmann 1968). Therefore, macro-surface hardness was limited by the critical stress of single cell walls. For the impregnated/control samples of Scots pine and beech samples, the depths of indentation of the steel ball on the surface were respectively presented to 0.85/0.82 mm, 0.60/0.48 mm, 1.25/1.27 mm and 0.76/0.66 mm (R/T). This fact showed that the surface hardness of treated sample had strengthened the first rows of cell walls. Moreover, the Brinell hardness of beech wood was still subject to the natural variability, in contrast to nearly no difference of tangential and radial surface hardness. When the load is applied across the fiber, it is absorbed by fiber walls bending into lumen and thereby giving a chance for the material to. Combining the more homogeneous diffusion of complexes in treated Scots pine than beech according to previous microscopic results, it progressively proved the aforementioned hardness effect. In fact, the changes in surface hardness may also reflect the changes in wood structure caused by the complexes. In other words, it concluded that there existed a cross-linking possibility of wood constituents via tannin-hexamine resin.

As for as the gluing properties, the investigations of shearing strength proved that pine WTNC had a better effect in contrast to control. According to 14080 (2013) requirements, wood failure occurred at around 6.0 N/mm^2 and the glueline can resist this stress. The successive wettability of beech WINC progressively proved this result, because the surface energy was significantly modified. Then it reduces the penetration of the water-based PVAc adhesives.

In some situations of exterior use timber components were subjected to wetting and may attain high moisture contents. At moisture contents greater than about 20%, fungal decay may occur (Christensen and Kaufmann 1965). Furthermore, exposure to fluctuating moisture conditions within the range 0 to 30% resulted in dimensional instability which can cause distortion of wood components in building (Bledzki and Faruk 2004). To improve

dimensional stability and to reduce the probability of fungal attack it is desirable to restrict the entry of water into wood.

Swelling behavior of WTNC in an environment of humidity variations presented little more unstable than control. In general, wood had the tendency to produce cracks during swelling. When it was objected to moisture, WTNC would afford fibre swelling by tannin-hexamine-boron resin and OMMT. The water-swellable OMMT formed self-change to lead to the dimension variety of wood matrix. Furthermore, polymers in the wood structure increased the swelling, which stressed the wood more and such treatment produced more or deeper cracks. The more substantial increase of swelling in radial direction could be explained considering that most of the easy accessible cells for the tannin polymer during impregnation were the latewood ones (Tondi et al. 2012). Moreover, this point had been investigated in previous studies of morphology. Therefore the water molecule will be adsorbed more easily in the earlywood, driving the swelling mainly in the radial direction.

The causes of shrinkage can be examined at molecular, ultrastructural, microscopic, and macroscopic levels (Ivković et al. 2009). At the molecular level, cellulose and hemicelluloses were responsible for desorption of water molecules, while lignin and extractives were retarding water penetration into cellulose. At the higher levels of wood structure, shrinkage of wood cells was considered to be dominated by tracheid wall thickness, lumen shape, effects of rays and bordered pits, and by the disposition of microfibril angles. In multi layers of wood with variable shrinkage properties (e.g. earlywood and latewood, or juvenile and mature wood), stresses develop from restraints between layers (Cave 1972, Pang 2002, Ivković et al. 2009). In current study, complexes of tannin-hexamine-boron resin and OMMT could lost moisture content to pull wood cell, which had been filled in cell lumen and on cell wall. Therefore, the shrinkage of WTNC was accelerated.

A preservative efficiency of complexes of tannin-hexamine-boron resin and OMMT can protect the wood (unleached) against biodegradation and moreover imbue the wood with any fire protection. About silicate-containing compounds, Levan (1984) indicated that sodium silicate act as a physical barrier, which can retard both smoldering combustion and flaming combustion by preventing the flammable products from escaping and by preventing oxygen from reaching the substrate. These barriers also insulate the combustible substrate from high temperatures. Miyafuji and Saka (2001) indicated that this enhanced fire resistance was assumed to be due to chemical and physicochemical effects, such as dehydration and carbonization of wood by silica gel.

Combustibility of fire-retardant wood depended on a number of factors such as the type of wood and retardant used for preparation of composite, its density, structure, thermal conductivity, and humidity. Fire behavior of wood was studied using the oxygen consumption cone calorimeter technique. Heat release rate (HRR) measured by cone calorimeter, represented a quantity of heat released by burning materials per unit area and time. Peak heat release rate (PHRR) expressed the maximum intensity of fire indicating the rate and extent of fire spread. The structural integrity of the material relied on mass loss rate. Besides, fire risk parameters as discussed earlier, the evolution of carbon monoxide and smoke were the most important hazard to life during fire and were discussed using the term. Therefore, in cone calorimeter test, the incomplete combustion products, such as carbon monoxide and smoke, were also measured and recorded.

Incorporation of clay produced an excellent barrier effect, preventing dripping and promoting char formation and hence improving the thermostability of the prepared composites (Camino et al. 2005). The char layers of individual clay improved the flame-retardant properties. Char protected the bulk of the sample from heat and decreased the rate of mass loss during thermal decomposition, thus providing an improved flame resistance (Deka et al. 2011). This gave relatively high thermal insulation capability to WTNC, which had been confirmed by excellent thermal conductivity results of beech wood. However, this excellent was induced into pine wood because softwood was difficultly impregnated to lead to low OMMT concentration.

The important parameter of SEA was negative values at the end of combustion. Indeed, the value was the more negative, the extinction was the stronger. The negative value was that further specimen burning was destroying smoke. While a certain amount of smoke may be destroyed by the heater under these low oxygen, non-flaming conditions, it was more possibly that smoke was decreased.

The MLR curves were identical to the HRR curves, so it was evident that the reduction of the MLR was the primary parameter responsible for the lower HRR of the composites.

Initially consider the relative differences in the thermal decomposition of sodium montmorillonite and OMMT. Greene-Kelly (1957) considered the montmorillonite differential thermal curve in two parts: (a) the free water and interlayer water region in the temperature range 100–300 ℃; (b) the structural water (bonded OH that undergoes dehydroxylation) region in the temperature range 500–1000 ℃. Obvious differences were observed for the pyrolysis behavior of BTNC samples with comparison with controls. On addition of OMMT, there was an improvement in thermal properties. Clay can act as a heat sink and mass transport barrier for the volatile products generated during decomposition.

5.5 Conclusions

Based on the results from this study, several conclusions were draw as follows：

(1) The preparation of organophilic OMMT was very successful, while MMT was modified with a compound including C_{16} alkyl quaternary ammonium cation.

(2) The tannin resin synthesized in the laboratory can effectively intercalate into OMMT to make its gallery distances increase markedly and even make its silicate layers exfoliated.

(3) FTIR analyses suggested that OMMT and wood interacted via certain chemical linkages in WTNC.

(4) XRD analysed indicate that the crystallinity degree of wood in WTNC decreased.

(5) Microscopic picture for WTNC indicated the complexes of tannin resin and OMMT existed different wood cell. SEM graphs for WTNC showed that some OMMT grains block in wood cell lumen, some OMMT layers adhered to the inner surface of wood cell walls and some exfoliated OMMT layers even insert into wood cell walls

(6) Physical and mechanical properties of WTNC were modified. By comparison with control, compression strength of treated Scots pine and beech increased; water absorption of treated Scots pine was improved when beech WTNC complicating; dimensional variation of treated wood did not have less stability during being placed in the water and water vapor; gluing ability of treated beech seemly decreased when water wettability was enhanced.

(7) Fungi and termite resistance of Scots pine WTNC were ameliorated, even if being subject to leaching. However, active ingredients in beech WTNC didn't resist the leaching.
(8) Fire retardant of WTNC was complicatedly altered. Heat release rate of control was higher than treated Scots pine wood before appearing the second peak of heat release, but afterward the heat release rate of control decreased to be lower than treated Scots pine wood. Whereas heat release rate of treated beech wood was always lower than control. Total smoke release of treated Scots pine wood was always less than control, which existed a variable effect to treated beech. Other smoke parameters expressed an impercipient effect.
(9) The effects of TGA proved that the onset temperature of the heat degradation slightly increased in the presence of complexes of tannin resin and OMMT. This implies that the thermal insulation of complexes had been enhanced. The analyses of simultaneous DSC–TGA also proved this result.

6. Life cycle assessment of tannin-boron preservative

6.1 Introduction

To achieve sustainable living, communities must balance the environmental, health, societal, and financial impacts associated with what we produce, use, and discard. Especially since the 1960s, the issue of environmental awareness has become increasingly important, leading to the creation of numerous regulations and laws, and leading to an increase of academic and scientific knowledge concerning this worldwide concern. So far, extreme restrictions have been applied to some timber preservatives in wood protection industry: such as, pentachlorophenol, creosote, as well as CCA (91/173/CEE; 98/8/EC; 2003/2/EC 2011/71/EU). Tannin-boron (TB) wood preservatives (as described in Chapter 3) based on the associations of tannins and boric acid are known for their high resistance against biological attacks, fire and leaching as well as for their good mechanical properties (Thevenon et al., 2009; 2010; 2011; Tondi et al, 2012a; 2012b). These properties promoted these formulations for being a candidate for the protection of green buildings. As a consequence, TB wooden products present an extended service life compared to boron compounds standing alone, and were designed to be environmentally friendly wood protection systems. So far, the TB products have been evaluated from a technical point of view and not for their potential environmental impact. Being so, it is vital that the environmental aspects of TB systems are taken into account and that more studies are made in order to successfully overcome the problem of TB preservative impacts on the environment.

Life cycle assessment (LCA) is a relatively holistic framework that exists today to help us understand the many ways in which a product or service could impact the environment, because LCA forces a rational examination of many indicators throughout material and product manufacture, use, and end of life.

Thus, LCA naturally emerges as a very useful tool in the evaluation and interpretation of TB environmental impacts. The LCA environmental tool has been used in this work to analyse and evaluate the environmental impacts of the TB-treated wood throughout its life cycle, from a cradle-to-grave perspective. In order to do so, the Simapro software version 7.1.8 (PRé Consultants bv) has been used, along with the Ecoinvent database, taking into account the TB manufacturing, use, and end of life phases. This assessment has been performed mainly using the environmental assessment method of ReCiPe Midpoint, although the method of Cumulative Energy Demand (CED) has also been used, to provide additional insights of energy consumption.

6.2 Methodologies

6.2.1 Goal and scope definition

This study analyses the environmental impacts of producing TB preservative and comparatively introduces the cradle-to-grave life cycle environmental impacts of TB-treated timber as landscaping materials, and uses LCA to quantify such impacts. Indeed, according to

the performances of TB products (Thevenon et al., 2009; 2010; 2011; Tondi et al, 2012a; 2012b, Chapter 3), it appeared reasonable to consider TB treated wood for outdoor, above ground end-use (Use Class 3) (EN 335, 2013) as landscaping material.

While this gives a well-defined scope for LCA from the product fabrication point of view, the raw materials production of tannin also is justified in term of the different process conditions. The environmental impacts of concrete product and treated timber are assessed throughout their life cycles, from the extraction of the raw materials through processing, transport, use as landscaping, reuse, and recycling or disposal of the product. Namely, three sets of LCA are conducted in this research:

(1) Based on water-extraction method proposed by Vieira (Vieira et al., 2011),

(2) Comparison of the wood preservatives: inorganic salt containing Cr (Cr), alkaline copper quaternary (ACQ) and TB (as described in Chapter 3, tannin concentration 10% being only considered for the LCA).

(3) Comparison of concrete product and three treated wood products with Cr, ACQ and TB in service for estimated 30 years.

All various scenarios are based in France (Europe). This study was performed using LCA methodologies in a manner consistent with the principles and guidance provided by the International Organization for Standardization (ISO, 2006E) in standards ISO 14040 and 14044. SimaPro version 7 was used for lifecycle modelling and impact assessment calculations.The inventory data are primarily extracted from the ecoinvent 3.01 LCA database (Ecoinvent Centre, 2013) and analysed using the ReCiPe (Goedkoop et al, 2009) and CED (Frischknecht et al, 2003) impact assessment methodologies. Together these cover a broad range of environmental, human health and resource depletion-based impact factors.

6.2.1.1 Functional unit

The functional unit (i.e. the unit against which the results are presented) of the study is one kg of material in the case of the wood preservative scenarios and 1m^3 of landscaping material (i.e. concrete or treated wood) for the subsequent scenarios. The life cycle stages considered are the material manufacture, the transport from production plant to landscape site, and the final disposal of the landscaping product. All inputs and outputs are consistently based to these functional units.

6.2.1.2 System boundaries

The cradle-to-grave life cycle stages of wooden landscaping materials considered in this research are illustrated in Figure 6-1, and system boundaries include the following life-cycle activities. Specially, processes including inputs and outputs related to burning wood biomass to dry lumber, use of electricity in saw mills, and transportation-related inputs and outputs were apportioned per functional unit.

(1) Production of timber and preservatives. The dominant species is Scots pine (*Pinus sylvestris*). The production of wood grew on French forest land at average forestry intensity, milled to dimensions, kiln-dried, and shaped at the local lumber mills. Tannins are supported by an Italian factory, boric acid in TB is commercial and purchased from a company in Montpellier; and then other preservatives are representative of European wood-preserving plants for treatment. It is noticed that cold-extraction process of tannin is referred to Vieira et

al (2011), from which the consumption of process electricity and transport ton-kilometers are calculated.

(2) Timber treating stage.

(3) Service-life of preservative-treated timber when used as landscaping materials. The treated products are classified Use Class 3 (UC3) (EN335, 2013)

(4) Preservative-treated timber disposal stage. The legislations of Commission Directive outline restrictions on the treated waste wood (TWW) disposal, and then these scenarios are modelled for three preservatives involved in this study: TB TWW is recycled, ACQ TWW is landfilled, and Cr TWW is incinerated. Especially, considering the composition of TB treated wood, recycling them for panel industry, as a particleboard with tannin glue (Pizzi, 2015) is an option.

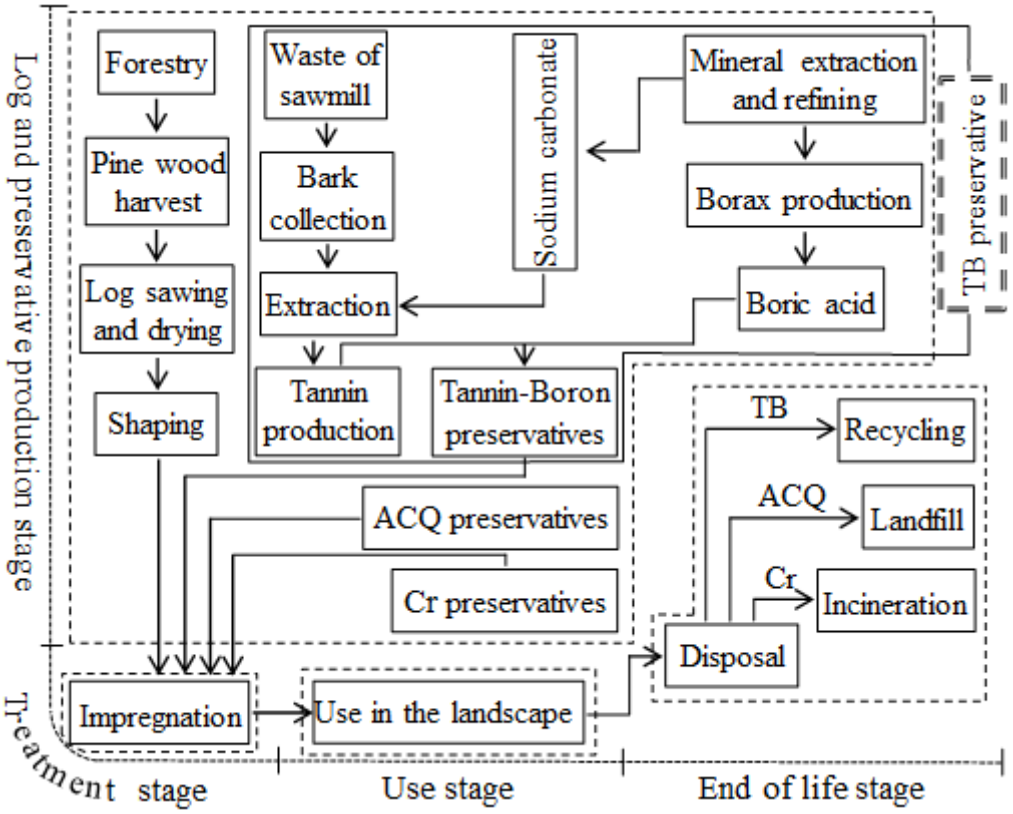


Figure 6-1 General flowchart for the life cycle of treated timber as landscaping material

Comparable cradle-to-grave LCA is available for concrete landscaping materials through the Ecoinvent life cycle inventory database. A representative concrete product design has been assumed: the concrete landscape equivalent to a C3 wooden landscape is likely to be appropriate during the service life. Concrete landscaping components include water, cement, sand, aggregate and admixture. The landscape casting process includes electricity, diesel and water. Concrete landscape manufacturing components transport to the casting plant is modeled as if by truck. Transportation of outbound precast concrete product to the use site also is modeled as if by truck. Post-use transport is assumed by truck as well. Transport distances to produced site in France were assumed for each stage. This LCA models 100% of used concrete landscape as landfill disposed.

6.2.2 Life cycle inventory (LCI)

Data used for the present study focus on the landscaping materials of inputs from technosphere, i.e. energy, materials and services. LCI has been segregated to compare the environmental impact of the various scenarios based on the results of the same boundaries. These data have been obtained by the combination of different sources and considering the functional unit previously established. Mainly, French data have been used, in other cases, European data supported by Ecoinvent v. 3.01 database (2014) was used. The data which were selected from French databases had the following requirements: it was to represent a relatively new technology, data based on laboratories, industries or processes in France, data from the latest time possible. The calculations, specifically for tannin production, TB and ACQ, were based on literature reviews, whereas the majority of parameter values were derived from verifiable literature resources and statistical data on relative production and utilization.

Table 6-1 Detailed LCI of 1kg TB preservatives

Product materials	Process	Amount	Unit	Information reference
Bark	Harvest	1.07	m^3	Vieira et al, 2011 and Li et al, 1998
Water	Extraction	5.91	kg	Vieira et al, 2011
Sodium carbonate	Extraction	0.51	kg	Vieira et al, 2011
Boric acid	Manufacture	0.02	kg	Data obtained from the experiment.
Hexamine	Manufacture	0.006	kg	Data obtained from the experiment.
Water	Manufacture	0.83	kg	Data obtained from the experiment.
Sodium hydrate	Manufacture	0.005	kg	Data obtained from the experiment.
All materials	Transport	0.13	tKm	The chemical dealer is assumed to be 100km distance from the production site. Tannin is assumed to be fabricated by an Italian factory 500km from site. The weight of each unit component considered is affirmed in this table 1.
Electrical energy	Manufacture	0.063	kWh	Figures were based on average useage of laboratory-scale stirrer (Hopkinson et al, 2011). It was assumed that the mixture is stirred for 10 minutes to 1kg TB preservative production. Data for the use of grid electricity is specific to the French grid.

Notably, the approach had a few limitations. The tannins extraction process was considered as described by Vieira et al. (2011) as no other option was available in the used databases

(chemicals being generally under-represented in LCI data, Campbell Skinner, personal communication). It was the only scientific contribution describing all the inputs needed to make a model. Nevertheless, it must be underline that extraction tannins used can be done through different ways in industry: using hot water in South Africa and Tanzania or 0.5%-1% sodium bisulphite in Brazil for wattle tannins, or, using 1%-2% sodium bisulphite and 0.5% sodium bicarbonate for quebracho tannins. The TB formulations used were based on mimosa tannins (Pizzi, personal communication). Moreover, in the data of tannin and TB used in this study, partial technical parameters cannot be involved in the industries because of the TB formulations being at experimental stage. It was assumed that the product flows included in the process-LCA were included completely. Tables 6-1 provide details of the aspects considered within the LCI TB. Analytical tools for testing the completeness of inventory data require company level data, which were unfortunately not available. However, it is known that tannin resources come from the forestry by-products. Especially, since the life cycle assessment inventory was very thorough, errors in the amounts of raw materials were assumed to be small. Therefore the following results in this study can be considered as accurate and reliable, for the parameters and scenario defined here. Any change in the parameters (tannin extraction in particular) and scenario would impact the final assessment.

6.2.3 Life cycle impact assessment (LCIA)

The assessment of environmental impacts of individual emissions and resource depletion is the sum of the impact generated from each scenario. These impact categories to analyze in this study were selected considering the current energy and environmental problem in France/Europe. This study uses combined life cycle impact assessment methods, CED (Cumulative Energy Demand) and ReCiPe, which are relatively new and have not been used in wood preservation domains.

The ReCiPe method for this LCIA, like many other reports on LCIA similar to the Eco-indicator 99 and CML 2002 methods, provides a tool to calculate life cycle impact category indicators (Goedkoop et al, 2009). ReCiPe comprises two sets of impact categories with associated sets of characterisation factors, and it is one of the most updated methods, combining midpoint and endpoint methodologies in a consistent way (Goedkoop et al, 2009). In this study impacts were assessed at the midpoint level since it has less uncertainties and value choices than the endpoint level, so then eighteen impact categories are addressed at the midpoint level. Furthermore, in order to decline a degree of uncertainty in the knowledge of the mechanisms which lead to climate change and other environmental impacts, ReCiPe develop three versions of individualist (I), hierarchist (H) and egalitarian (E) on the basis of the cultural perspectives theory of Thompson (1990) and the three perspectives reflect different degrees of optimism for the causality process-effect by considering different time frames, rates of adaptation, etc. (Goedkoop et al, 2009) In the present study, the hierarchist perspective is chosen for the calculation of midpoint impact.

It should be noted that the applied LCIA method for energy-related issues evaluate the primary energy use through the life cycle of the product. CED method states the entire demand is assessed as the primary energy, which arises in connection with the production, use and disposal of a product or service, or which may be respectively attributed to it through cause (Zabalza Bribián et al, 2011). Thus, the CED method is chosen to analyze a general

view of the energy-related environmental impacts in a life cycle, and it can also deliberate the electricity in France and distinguish between non-renewable (fossil and nuclear) and renewable primary energy use (hydraulic, biomass, wind, solar and geothermal).

6.2.4 Sensitivity parameters

Sensitivity analysis was used to explore the impact of varying two of the key parameters in the tannin production process, specifically the ration of liquor to bark and the sodium carbonate concentration. As such, the lifecycle was re-modelled using the revised parameters so that the lifecycle results could be compared. Sensitivity parameters in which they were combined for the mentioned purpose are described in Table 6-2.

Table 6-2 Processes of cold-extraction tannin

N °process	Liquor / bark ratio	Na_2CO_3 concentration
1	15:1	8.0%
2	12:1	7.5%
3	7.5:1	7.0%

6.3 Results and discussion

6.3.1 LCIA of procedure network for 1kg TB preservatives

The assessment of producing TB attained by ReCiPe method is shown in a generic figure for the hierarchism where one can see the main contributions of climate change to the entire process, and this process tree also elaborates the contribution of energy consumption during the process. In the figure 6-2, the contribution counts of primary processes are visible, but that

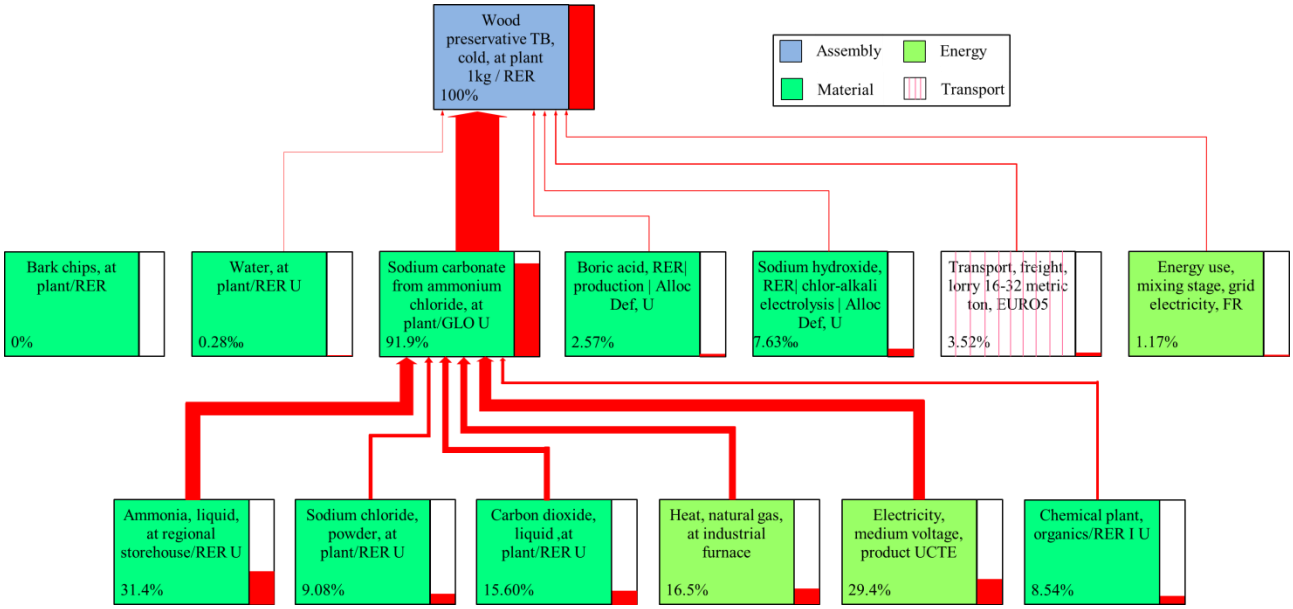


Figure 6-2 Dendrogram from SimaPro exposing the main contributions of TB process to global warming potential (GWP)

of sub-processes that contribute less than that level are ignored (their contribution counts in the result of course), namely cut off below 8%. The biggest emission sources regarding

climate change potential can be found in figure 6-2, which shows parts of the simulations done by Simapro. This figure allows us to focus on the "Na_2CO_3" sub-process which is used for tannin extraction (Vieira et al, 2011). This model illustrates clearly that the fabrication of sodium carbonate is the main contributors to the GWP of this sub-process. Climate change is also significantly affected by those sub-processes of sodium carbonate, namely 31.4% GWP of produce-need liquid ammonia and 29.4% GWP of electricity energy. However, considering that there is a biais between our model and the mimosa tannin extraction in industry, the impact calculated here should not be taken for granted.

Subsequently we took a look at the relative impact to the energy consumption impactors of TB production. As usual with reference to the functional unit, the CED environmental assessment method was used. Moreover, the evaluated results of primary energy use are shown in Figure 6-3. It is possible to have a generic idea of the different types of energy used throughout the TB process, as well as the comparative impact of each energy type demand. Noticeable in this figure is again the predominant presence of the impact from the "Na_2CO_3" sub-process, excluding the depletion of renewable biomass. Nevertheless, we mention here some "striking" facts from this figure, like the high contribution of the electricity energy to the non-renewable nuclear indicator, as well as of the bark to the renewable biomass. France derives about 75% of its electricity from nuclear energy (Finon and Romano, 2009); therefore, electricity use dominates a remarkable situation in the non-renewable nuclear. The effect of fully occupied renewable biomass is bark, which probably due to the manufacturing material of only plant.

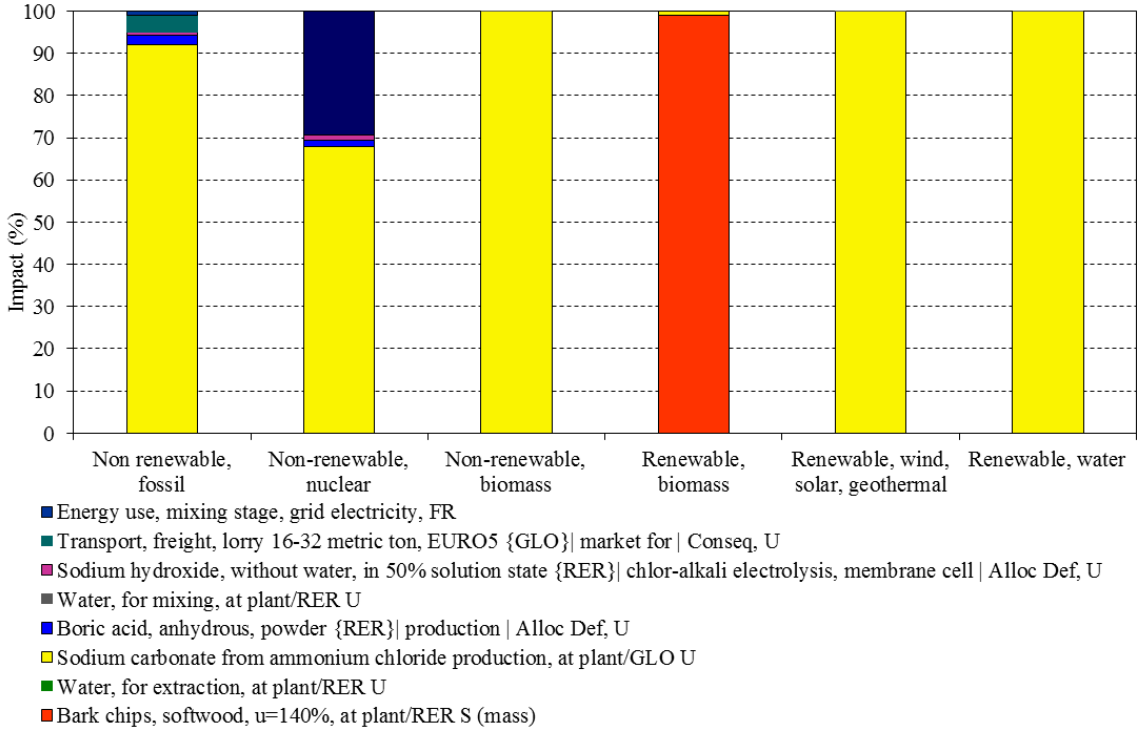


Figure 6-3 Contribution of impact categories to the single score for TB by CED method

6.3.2 Comparison of selected landscaping materials

The table 6-3 currently keeps track of 18 acronyms of the midpoint impact assessment for ReCiPe method. Afterward, all similar acronyms would refer to table 6-3.

Table 6-3 List of acronyms for ReCiPe method (midpoint) impact category

Acronym	Impact category	Acronym	Impact category
CC	Climate change	OD	Ozone depletion
TA	Terrestrial acidification	FEP	Freshwater eutrophication
MEP	Marine eutrophication	HT	Human toxicity
POF	Photochemical oxidant formation	PMF	Particulate matter formation
TET	Terrestrial ecotoxicity	FET	Freshwater ecotoxicity
MET	Marine ecotoxicity	IR	Ionizing radiation
ALO	Agricultural land occupation	ULO	Urban land occupation
NLT	Natural land transformation	WD	Water depletion
MD	Metal depletion	FD	Fossil depletion

Absolute results are reported in Table 6-4. Figure 6-4 shows the characterized results for each impact category. That is to say that the results for each impact category are presented on a percentage basis, with the highest scoring scenario represented as 100% and the remaining three scenarios scaled against this. This allows for comparison of relative scale across the various impact categories.

Table 6-4 Impact categories for 4 landscaping materials based on ReCiPe-characterization results per m^3 material

Impact category	Unit	LM1	LM2	LM3	LM4
CC	kg CO_2 eq	$1.725 \cdot 10^{2}$	$5.557 \cdot 10^{2}$	$6.244 \cdot 10^{2}$	$1.998 \cdot 10^{2}$
OD	kg CFC-11 eq	$7.119 \cdot 10^{-5}$	$1.848 \cdot 10^{-5}$	$8.455 \cdot 10^{-5}$	$2.194 \cdot 10^{-5}$
TA	kg SO_2 eq	1.124	2.464	9.838	$9.416 \cdot 10^{-1}$
FEP	kg P eq	$1.601 \cdot 10^{-1}$	$7.509 \cdot 10^{-2}$	2.081	$8.088 \cdot 10^{-2}$
MEP	kg N eq	$5.839 \cdot 10^{-1}$	$1.003 \cdot 10^{-1}$	$5.773 \cdot 10^{-1}$	$3.894 \cdot 10^{-1}$
HT	kg 1,4-DB eq	$3.228 \cdot 10^{2}$	$1.065 \cdot 10^{2}$	$4.803 \cdot 10^{3}$	$8.032 \cdot 10^{1}$
POF	kg NMVOC	1.273	2.539	4.101	1.212
PMF	kg PM10 eq	$4.327 \cdot 10^{-1}$	$9.949 \cdot 10^{-1}$	3.357	$3.649 \cdot 10^{-1}$
TET	kg 1,4-DB eq	$4.248 \cdot 10^{-2}$	$2.618 \cdot 10^{-2}$	$3.452 \cdot 10^{-1}$	$2.541 \cdot 10^{-2}$
FET	kg 1,4-DB eq	5.875	2.609	$1.118 \cdot 10^{2}$	2.183

(continued)

Table 6-4 *(concluded)*

MET	kg 1,4-DB eq	5.989	2.837	$1.142 \cdot 10^{2}$	2.221
Impact category	Unit	LM1	LM2	LM3	LM4
IR	kBq U235 eq	$2.105 \cdot 10^{2}$	$2.975 \cdot 10^{1}$	$6.624 \cdot 10^{1}$	$6.352 \cdot 10^{1}$
ALO	m^2a	$2.312 \cdot 10^{3}$	$2.357 \cdot 10^{1}$	$2.335 \cdot 10^{3}$	$2.313 \cdot 10^{3}$
ULO	m^2a	$2.921 \cdot 10^{1}$	$1.246 \cdot 10^{1}$	$4.095 \cdot 10^{1}$	$2.796 \cdot 10^{1}$
NLT	m^2	$2.271 \cdot 10^{-1}$	$-5.808 \cdot 10^{-3}$	$3.306 \cdot 10^{-1}$	$2.670 \cdot 10^{-1}$
WD	m^3	$1.359 \cdot 10^{3}$	$6.987 \cdot 10^{2}$	$2.533 \cdot 10^{3}$	$6.590 \cdot 10^{2}$
MD	kg Fe eq	$8.234 \cdot 10^{1}$	$4.346 \cdot 10^{1}$	$2.371 \cdot 10^{3}$	$1.936 \cdot 10^{1}$
FD	kg oil eq	$5.291 \cdot 10^{1}$	$1.038 \cdot 10^{2}$	$1.470 \cdot 10^{2}$	$6.539 \cdot 10^{1}$

Note: LM1 refers to landscaping material of $1m^3$ ACQ treated wood (ex-AP), LM2 refers to landscaping material of $1m^3$ concrete block, LM3 refers to landscaping material of $1m^3$ Cr treated wood (ex-AP), and LM4 refers to landscaping material of $1m^3$ TB treated wood (ex-AP).

Analysing table 6-4 and figure 6-4 (Annex H), the life cycle of Cr treated wood scores highest on all impact factors except on marine eutrophication and ionizing radiation, while TB-treated wood has the lowest environmental impact on most impact categories. In terms of climate change, the emission factor of TB-treated wood is 199.8 Kg CO_2 eq, slightly more than ACQ-treated wood (172.5Kg CO_2 eq), and much less than the case of Cr-treated wood and concrete (respectively 624.4 Kg CO_2 eq and 555.7 Kg CO_2 eq). The most affecting category for TB treated wood is agricultural land occupation, and it is not surprising due to raw materials input producing in the land. In total, the environmental burdens of Cr treated wood are severe, and the concrete landscaping material is general excluding resources depletion. Comparing those TB and ACQ treated wood, 2 impact categories out of 18 present some interesting, viz. climate change and fossil depletion. Focusing attention on global warming potential and fossil depletion: these weaknesses of TB treated wood were indicated due to the sodium carbonate, however, the distance of contributor based these impact categories was not so great between TB treated wood and ACQ treated wood.

Regarding four landscaping materials, energy consumption was relatively high compared to other impact categories according to ReCiPe method. A CED is calculated based on the higher heating value and distinguishes renewable and non-renewable energy sources (Frischknecht et al, 2007). Non-renewable CED is very important to assess the depletion of fossil energy resources or the renewability of a system (Malça et al, 2006). As can be seen in Fig. 6-5 (Annex I) and Tab. 6-5, there is an attention in four landscaping materials, namely consuming non-renewable energies of TB treated wood. The results show that the concrete block is the most significant due to no consummation of non-renewable energies. It can also be noted that there is a significant difference in non-renewable CED results between the

various landscape scenarios: the nuclear energy of ACQ treated wood is highest, and France is a country of nuclear electricity.

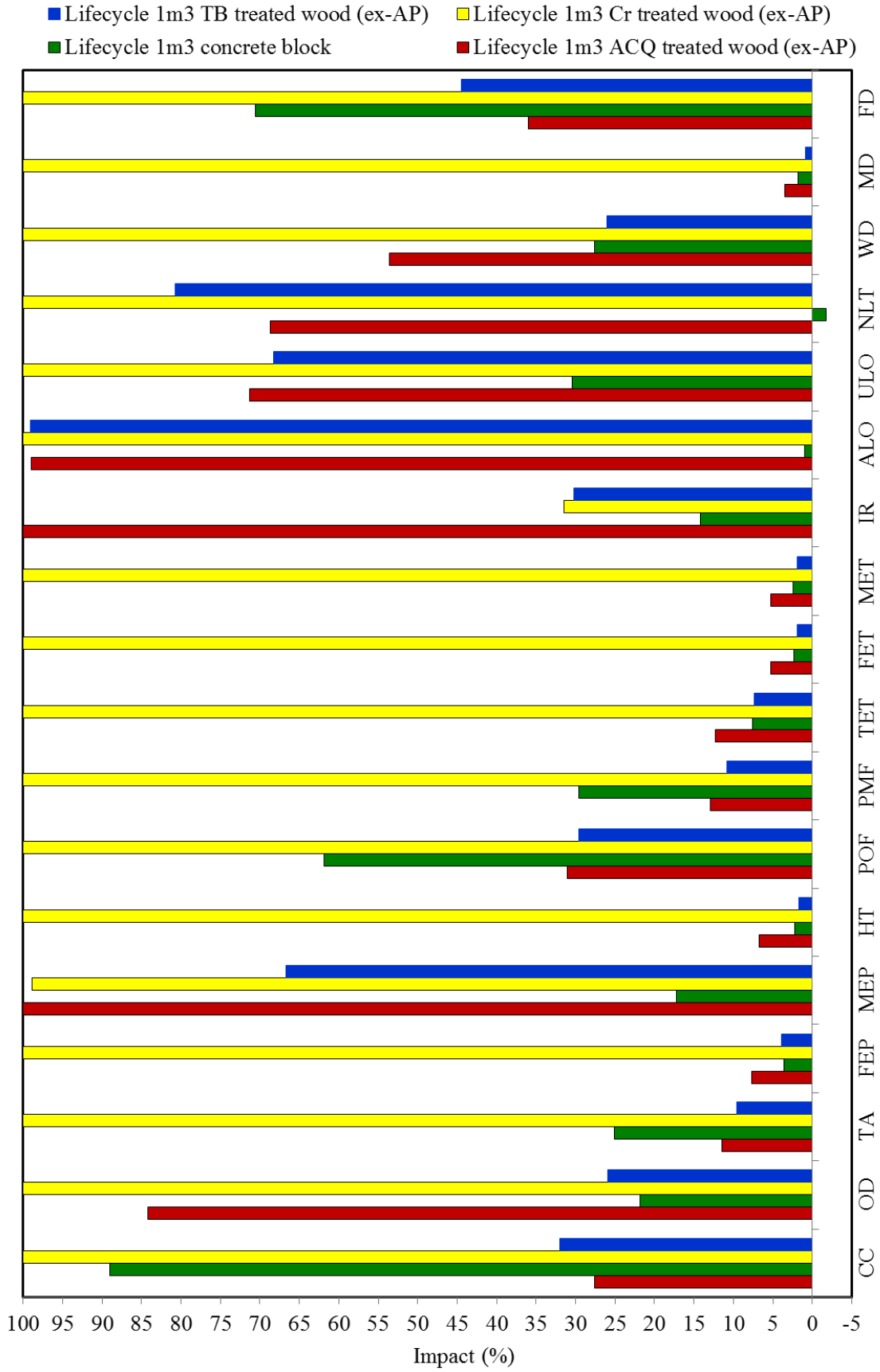


Figure 6-4 Contributions from impact categories of ReCiPe method to each per m^3 material

Table 6-5 Impact categories for 4 landscaping materials based on CED-characterization results per m^3 material

Impact category	Unit	LM1	LM2	LM3	LM4
Non-renewable, fossil	MJ	$2.363 \cdot 10^3$	$4.639 \cdot 10^3$	$6.613 \cdot 10^3$	$2.942 \cdot 10^3$
Non-renewable, nuclear	MJ	$2.655 \cdot 10^3$	$2.157 \cdot 10^2$	$6.988 \cdot 10^2$	$6.709 \cdot 10^2$
Non-renewable, biomass	MJ	$4.659 \cdot 10^{-3}$	0.000	$4.263 \cdot 10^{-3}$	$5.786 \cdot 10^{-3}$
Renewable, biomass	MJ	$9.207 \cdot 10^3$	0.000	$9.206 \cdot 10^3$	$1.119 \cdot 10^4$
Renewable, wind, solar, geothe	MJ	3.464	0.000	3.191	8.611
Renewable, water	MJ	$3.558 \cdot 10^1$	0.000	$2.432 \cdot 10^1$	$6.487 \cdot 10^1$

Note: LM1 refers to landscaping material of $1m^3$ ACQ treated wood (ex-AP), LM2 refers to landscaping material of $1m^3$ concrete block, LM3 refers to landscaping material of $1m^3$ Cr treated wood (ex-AP), and LM4 refers to landscaping material of $1m^3$ TB treated wood (ex-AP).

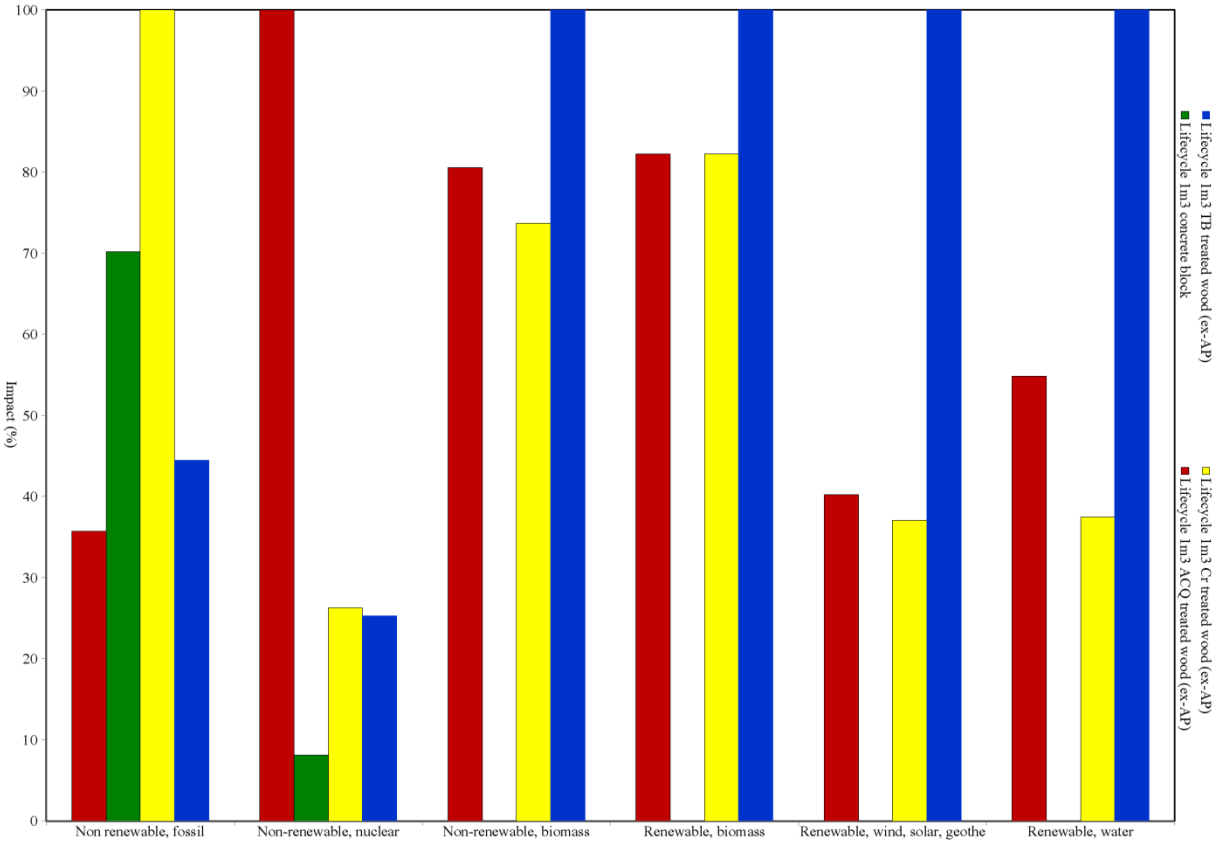


Figure 6-5 Contributions from impact categories of CED method toward each per m^3 material

6.3.3 Sensitive analysis

It is considered that the outcome of the LCA can be quite heavily dependent on some of the assumptions. This does not need to be a problem as long as the conclusions of LCA are stable. From Fig. 6-6 and 7, those environmental burdens and energies consummation have changed following the liquor and Na_2CO_3 concentration. Being so, the modelling comprised also the

difference in energy consumption among the three processes that had been modelled for this study. The life cycle impact assessment results of tannin extraction also present significantly different, being that for the climate change the uncertainty range is between -38.14% and 13.71%, regarding the 0.451 Kg CO_2 eq used to model the process 2. Generally, the treatments with varying proportions of sodium carbonate had different values of tannin extract; however treatment with 8% sodium carbonate provided the higher yield of condensed tannins, underlining the importance of utilizing this specific salt concentration in the extraction process (Vieira et al. 2011).

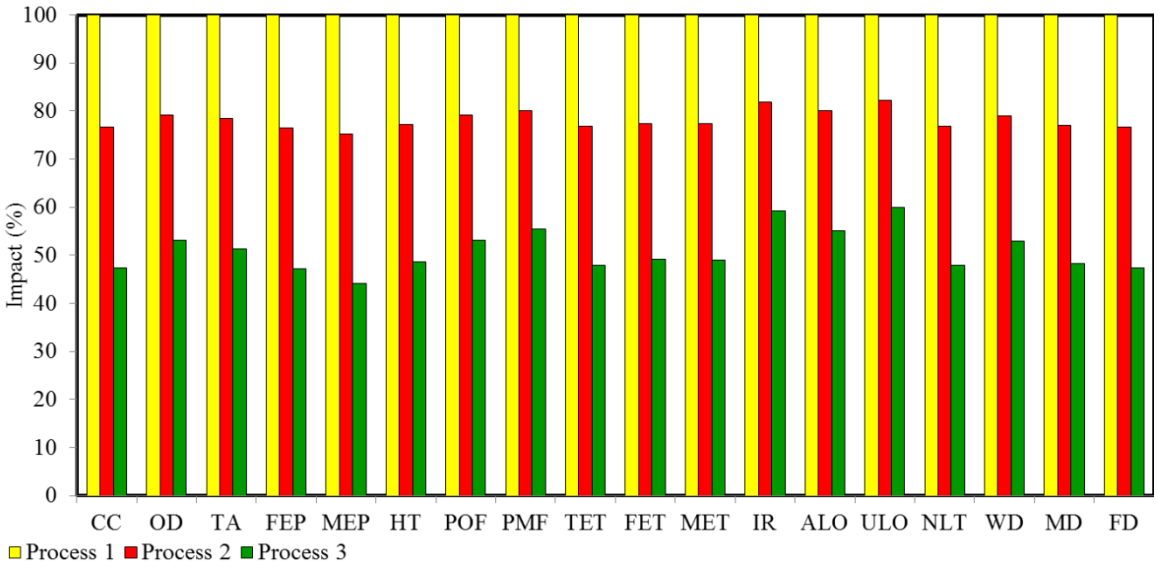


Figure 6-6 Comparing contributions from impact categories of ReCiPe method toward 3 processes of tannin extract

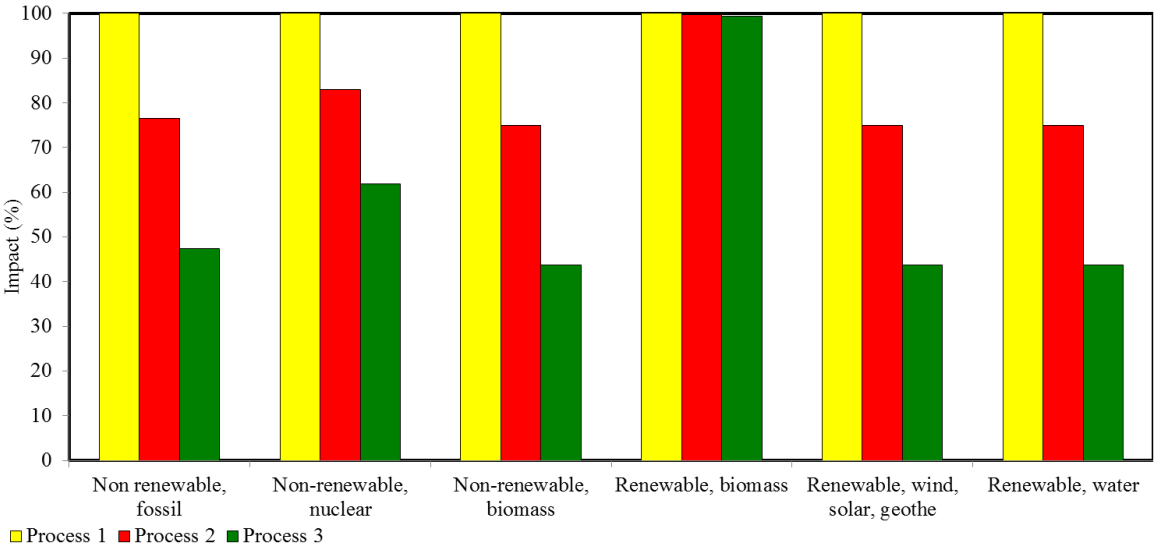


Figure 6-7 Comparing contributions from impact categories of CED method toward 3 processes of tannin extract

6.3.4 Limitation and recommendations

LCA is a comparison tool that examines the environmental impacts related to these landscaping materials by considering the potential exposure rather than the actual exposure. However, LCA has not an absolute ability to describe the studied system with a systematic

and comprehensible LCIA method. LCA deals with the cradle-to-grave assessment of these products, which is usually not covered by other assessment tools. The environmental impacts in LCA are calculated from a set of well-defined factors, which help simplify the studied problem and accelerate the analysis.

In the future, additional research is required in order to improve the quality and comprehensiveness of the new TB preservatives and other subsequent comparative LCA studies related to wood preservation formulation. The accuracy of this study could be improved by using full-scale TB treated production manufacturing input data, along with refining the tannin production process evaluation. With respect to sustainability of wood preservation, this comparison was based solely on environmental performance. Hence, in order to address the full scope of sustainable TB treated timber, life cycle costing, and life cycle sustainability assessment are techniques that could be employed in order to expand the analysis of TB formulation comparison to include a more complete sustainable treatment. Predominantly, the data used was laboratory wide and averaged over the entire Europe. Further research is also needed to determine TB preservative production data at industrial-scale. This would aid in providing an even clearer perspective of the comparative LCIA analysis.

6.4 Conclusions

LCA evaluating the environmental impacts of 4 landscaping materials from cradle to grave have been implemented. Considering the environmental benefits, concrete and Cr treated wood do not appear competitive landscaping materials from an environmental point of view.

The results calculated for the two LCIA methods show: the use of ACQ-treated lumber for landscape offers lower environmental impacts (CO_2 emission) than others, and TB-treated wood landscape consumes more renewable resources.

Although climate change was the most discussed impact category concerning the environmental concerns of landscaping materials, other categories were analysed in order to have an idea of their importance. In general the impact categories are limited to: non-renewable resources (with and without energy content), renewable resources (with and without energy content), global warming (CO_2 equivalents), acidification (kg SO_2 equivalents), ozone depletion (kg CFC-11 equivalents) and photochemical oxidant formation (kg ethane-equivalents), and then TB preservatives can be regarded a low-environmental impact formulation.

However, the influential parameters of tannin processing at industrial scale should now be investigated further, and eco-toxicological tests on TB treated wood must be carried out. Additionally, an economic analysis of the development of a commercially-viable tannin-boron preservative is crucial. Only then, a complete statement on whether TB is an eco-innovative way of mitigating climate change by extending carbon storage in treated wood, can be ascertained.

7. General conclusions and perspectives

Tannin, are widely distributed in plants and primarily used in wood adhesive, leather tanning, dyeing fabric, making ink, food industry and various medical applications (Pizzi 2006, Joseph and Nithya 2009, Ferreira et al. 2004, Khanbabaee and van Ree 2001, Ferreira et al. 2005).
Boron, as a water soluble wood preservative, is easily impregnated into wood and has the ability to diffuse into it. Due to this behavior, it is also readily leachable from treated wood when in outside exposure. Boron-based preservatives show high performances against wood decay fungi, and present a low toxicity to mammals and fish (Kabu and Akosman 2013). Anyway, to carry on using boron, one has to comply with the EC regulation and use it at very low level (below 5.5% w/w, 2008/58/EC).
Then, the challenge is to fix boron, in the form of boric acid, for a long term in wood in order to keep its biological and fire proofing performances outside.
In 1996, Pizzi and Baecker cast the first stone to launch the study for the environmentally friendly preservatives of complexes of boron with flavonoid tannins. It also inspired the fellow follower to sharpen this novel formulation. The technology exploited the tannin polymerization property and it consisted in infiltrating the activated oligomers of flavonoid in the wood with a successive in-situ polymerization catalysed by heat (Thevenon et al. 2009).
Original formulations based on tannins-hexamine-boron associations had shown outstanding preservation properties against biologic attack and fire and they had also shown improved mechanical properties (Tondi et al. 2012a, b, Tondi et al. 2013a). Unfortunately the tannin-treated timber was still quite highly affected by artificial and natural weathering exposures (Tondi et al. 2012c). All in all, such associations combining the effects of tannin and boron, and using boric acid at a very low level, observed the restrictions on the use of boron compounds and avoided boric acid leaching, and increased performances and service life of wood treated in this manner (Obanda et al. 2008).

7.1 Review of results

This study had considered the mix tannin-hexamine resin to complex boron in the form of boric acid, which sought the long-term and low-environmental impact wood preservatives and also investigated the properties of treated wood. The following conclusions can be made from studying the effect of different tannin-boron formulations and environmental impact.

7.1.1 Tannin-boron formulation

The first part of this work was inserted in a larger study dealing with tannin-hexamine-boron associations as wood preservatives. These formulations were proved efficient against biological attack after leaching, from a laboratory point of view (Thevenon et al. 2009, Tondi et al. 2012b). Our investigation was to test the residual biological activity after natural and artificial weathering. Due to the configuration of the weathering tests, only the termite resistance could be evaluated.
In the investigation of termite resistance, residual boron in weathered wood treated with

tannin-boron preservative was not enough to hinder biological deterioration after photoprotective treatments breaks cross-linked and inelastic tannin polymer networks. However, artificial-weathered and natural-weathered tannin-treated wood differently responded to termite attack: remained boron in wood after natural weathering can kill all termites. To die, the termites have to ingest treated wood, and in this case the amount of wood destroyed was high due to the low level of boron left. The wood blocks after artificial weathering presented a termite survival and attacked comparable with the controls, indicating that not active ingredient remained into the wood.

Although tannin-hexamine-boron formulations had very interesting properties as wood preservatives, they needed to be improved for outdoors applications.

Considering the evaluations and observations done on the wood treated with these systems, it was noticeable that the polymer created into the wood was rigid, leading to a different surface behavior of treated wood, and to splits and cracks when leached or weathered.

The following step of our study was to use a long flexible molecule, e-caprolactam, to integrate in our polymer complex to overcome this problem

7.1.2 Advanced tannin-boron formulation

From the results obtained in our experiments, we can conclude that the structure of tannin polymer did not change with additive of ε-caprolactam, but it was assumed from the chemical spectra that ε-caprolactam had successfully been connected on the branch of tannin polymer. This new polymer association was shown to be rather insoluble.

When these associations were used to treat the wood, the presence of ε-caprolactam did not really modify the retention of tannin and boric acid.

The colour of samples treated with tannin/boron/caprolactam still appeared brown.

The biological resistance of such treated wood was proved very performant in laboratory tests. Even after leaching according to EN84, the wood samples still presented a mass loss below 3% against the attack of very aggressive tropical strain *Antrodia*. The same behavior was shown also for a temperate strain, *Coniophora*. Termite resistance was also largely improved.

Unsterile soil-bed tests have shown that the durability of such treated wood was increased, and a good dose response behavior could be seen in the tests conducted in the Montpellier site.

Thus, the polymerization of tannin and hexamine included actively the ε-caprolactam in the network is effective and the boron fixation in the treated wood is enhanced. MOR and MOE of wood treated with tannin/boron/caprolactam preservative were not obviously altered, even if ε-caprolactam modified the rigidity of the tannin polymer.

Fire retardancy performances of specimens treated with tannin/boron/caprolactam formulation, even if lower that the first original formulation (no ε-caprolactam), remained better that the controls.

ε-Caprolactam could be supplied lasting protection against wood degradation in outdoor exposures.

7.1.3 Wood nanocomposite based tannin polymer and montmorillonite

The third part of our study was to explore the possibilities of using modified nanoclay (montmorillonite) in association with tannin-boric acid (in the presence or not of hexamine) to produce a so-called Wood Tannin NanoComposite.

The tannin-hexamine-boron resin synthesized in the laboratory can effectively intercalate into OMMT to make its gallery distances increase markedly and even make its silicate layers exfoliated.

FTIR analyses suggested that OMMT and wood interacted via certain chemical linkages in WTNC, and then XRD analysed indicate that the crystallinity degree of wood in WTNC decreased.

Microscopic observations for WTNC indicated the complexes of tannin resin and OMMT existed in different wood cell. SEM pictures for WTNC showed that some OMMT grains block wood cell lumen, some OMMT layers adhered to the inner surface of wood cell walls and some exfoliated OMMT layers even insert into wood cell walls

Physical and mechanical properties of WTNC were modified. By comparison with control, compression strength of treated Scots pine and beech increased; water absorption of treated Scots pine was improved when beech WTNC behaved differently; behavior of treated wood towards water (dimensional stability with liquid and vapor water) was slightly deteriorated.

Fungal and termite resistance of Scots pine WTNC were ameliorated, even if being subject to leaching. However, active ingredients in beech WTNC did not resist the leaching.

Fire retardant of WTNC was complicatedly altered. Heat release rate of control was higher than treated Scots pine wood before appearing the second peak of heat release, but afterward the heat release rate of control decreased to be lower than treated Scots pine wood. Whereas heat release rate of treated beech wood was always lower than control. Total smoke release of treated Scots pine wood was always less than control, which existed a variable effect to treated beech. Other smoke parameters expressed an impercipient effect.

The effects of TGA proved that the onset temperature of the heat degradation slightly increased in the presence of complexes of tannin resin and OMMT. This implies that the thermal insulation of complexes had been enhanced. The analyses of simultaneous DSC – TGA also proved this result.

Associations between tannin-boric acid-hexamine-OMMT can effectively be used to treat wood samples. The obtained wood WTNC have their properties affected in different ways due to the treatment. Nevertheless, the most important parameter is probably the water behavior of the treated wood. WTNC appears to be able to retain more water than untreated wood, creating a worse case environment for wood protection.

7.2 Perspectives

Considering the 3 systems studied, the associations between tannin-hexamine-boron-caprolactam appear to have the highest potential to be developed as efficient wood preservatives.

It must be underline that the amount of boric acid used in these formulations are not higher than 0.5% w/w for the laboratory tests, and 3% w/w for the unsterile soil bed test. Thus, to overcome the termite attacks or to improve the durability in ground contact, it is still possible to increase the boron content of our formulations. If this is done, the complete balance of the formulation will have to be re-considered in order to keep fixing the boron efficiently.

However, tasks remained to be done to understand fully the mechanisms of these associations. The leaching waters obtained from our experiments have to be analysed for their tannins and

boron contents, the MOE and MOR after field testing have to be performed, and the results of their field test will also have to be compared. It should be also envisaged to test other wood destroying organisms.

Moreover, the environmental as well as the eco-toxicological profile of this product will have to be evaluated. Considering the balanced results obtained with the original formulation (tannin-boric acid-hexamine) from a life-cycle point of view, a life cycle assessment could be re-think with optimized parameters, in terms of tannins production impact and also by considering a different end-use of the wood (i.e. building material instead of landscaping material). Scaling up the treatment process (to pilot and industrial scale) will also be a crucial step for the development of these alternative, long-term wood preservatives.

References

2003/2/EC (2003) Restrictions on the marketing and use of arsenic (tenth adaptation to technical progress to Council Directive 76/769/EEC). European directive 2003/2/EC, 06/01/2003

2008/58/EC (2008) Amendment of 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification: packaging and labelling of dangerous substances. European directive 2008/58/EC, 31/12/2008

2011/71/EU (2011) Include creosote as an active substance in Annex I of the 98/8/EC. European directive 2011/71/EU, 26/07/2011

91/173/CEE (1991) Restrictions on the marketing and use of certain dangerous substances and preparations. European directive 91/172/CEE, 21/03/ 1991

98/8/EC (1998) Placing on the market of biocidal products. European directive 98/8/EC, 16/02/1998

Abdullah UH, Pizzi A, Rode K, Delmotte L, Zhou X, Mansouri HR (2013a) Mimosa tannin resins for impregnated paper overlays. *European Journal of Wood and Wood Products* 71(2): 153-162

Abdullah UH, Zhou X, Pizzi A, Merlin A (2013b) Note on surface quality of plywood overlaid with mimosa (*Acacia mearnsii*) tannin and melamine urea formaldehyde impregnated paper: effects of moisture content of resin impregnated papers before pressing on physical properties of overlaid panels. *International Wood Products Journal* 4(4): 253-256

Akbulut T, Kartal NS, Green F (2004) Fiberboards treated with N'-N-(1,8-Naphthalyl) hydroxylamine (NHA-Na), borax, and boric acid. *Forest Products Journal* 54(10): 59-64

Akong FO, Mutlu M, Pasc A, Cosgun S, Gérardin P, Gérardin-Charbonnier C (2013) Hydrogels obtained from an original catanionic system for efficient formulation of boron wood-preservatives. *International Biodeterioration and Biodegradation* 77: 123-126

Alexandre M, Dubois P (2000) Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Materials Science and Engineering: R: Reports* 28(1): 1-63

Amburgey TL, Freeman MH (2000) An update on the efficacy and performance of a copper naphthenate –borax preservative paste. In: Proceedings International Conference on Utility Line Structures, Fort Collins, CO. pp.33-37

Amburgey TL, Watt JL, Sanders MG (2003) Extending the service life of wooden crossties using pre- and supplemental preservative treatments. 15 year report. Crossties May/June 2003

Aranguren MI, Borrajo J, Williams RJJ (1982) Some aspects of curing novolac with hexamethylenetetramine. *Journal of Polymer Science: Polymer Chemistry Edition* 20(2): 311-318

Athanasiadou S, Kyriazakis I, Jackson F, Coop RL (2001) Direct anthelmintic effects of condensed tannins towards different gastrointestinal nematodes of sheep: in vitro and in vivo studies. *Veterinary Parasitology* 99(3): 205-219

AWPA (2005) American Wood-Preservers' Association Standard. P5: Standard for Waterborne Preservative. The executive director office of the federal register Washington, D.C

Azapagic A (2007) CCaLC2: Carbon calculations over the life cycle of industrial activities. The University of Manchester. Available from http://www.ccalc.org.uk/about.php

Bamber RK, Burley J (1983) The wood properties of radiata pine. Common wealth Agricultural Bureaux Sloough, England

Bariska M, Pizzi A (1986) The interaction of polyflavonoid tannins with wood cell-walls. *Holzforschung* 40(5): 299-302

Barnes HM, Armburgey TL, Williams LH, Morrell JJ (1989) Borates as wood preserving compounds: the status of research in the United States. The International Research Group on Wood Preservation, IRG/WP 89-3542. IRG Secretariat, Stockholm, Sweden

Barnes HM, Murphy RJ (1995) Wood preservation: the classics and the new age. *Forest Products Journal* 45(9): 16-26

Basso MC, Giovando S, Pizzi A, Celzard A, Fierro V (2013) Tannin/furanic foams without blowing agents and formaldehyde. *Industrial Crops and Products* 49: 17-22

Basso MC, Lacoste C, Pizzi A, Fredon E, Delmotte L (2014) MALDI-TOF and 13 C NMR analysis of flexible films and lacquers derived from tannin. *Industrial Crops and Products* 61: 352-360

Baysal E, Altinok M, Colak M, Ozaki SK, Toker H (2007) Fire resistance of Douglas fir (Pseudotsuga menzieesi) treated with borates and natural extractives. *Bioresource Technology* 98(5): 1101-1105

Baysal E, Kiyoka S, Yalinkilic MK (2004) Dimensional stabilization of wood treated with furfuryl alcohol catalysed by borates. *Wood Science and Techology* 38(3): 405-415

Baysal E, Yalinkilic MK (2005) A new boron impregnation technique of wood by vapor boron of boric acid to reduce leaching boron from wood. *Wood Science and Technology* 39(3): 187-198

Bendel P (2005) Biomedical applications of ^{10}B and ^{11}B NMR. *NMR in Biomedicine* 18(2): 74-82

Beyer G (2002) Nanocomposites: a new class of flame retardants for polymers. *Plastics, Additives and Compounding* 4(10): 22-28

Bledzki AK, Faruk O (2004) Creep and impact properties of wood fibre–polypropylene composites: influence of temperature and moisture content. *Composites Science and Technology* 64(5): 693-700

Böcük H, Türe C (2014) Phytoremediation possibilities of boron-contaminated environments by wild plants growing on boron reserve areas in Turkey. *Communications in Soil Science and Plant Analysis* 45(13): 1784-1798

Bodirlau R, Teaca CA, Spiridon I (2008) Chemical modification of beech wood: effect on thermal stability. *BioResources* 3(3): 789-800

Bolin CA, Smith S (2011a) Life cycle assessment of ACQ-treated lumber with comparison to wood plastic composite decking. *Journal of Cleaner Production* 19(6): 620-629

Bolin CA, Smith S (2011b) Life cycle assessment of borate-treated lumber with comparison to galvanized steel framing. *Journal of Cleaner Production* 19(6): 630-639

Bolin CA, Smith S (2011c) Life cycle assessment of pentachlorophenol-treated wooden utility poles with comparisons to steel and concrete utility poles. *Renewable and Sustainable Energy Reviews* 15(5): 2475-2486

Bolin CA, Smith S (2013a) Life cycle assessment of CCA-treated wood highway guard rail posts in the US with comparisons to galvanized steel guard rail posts. *Journal of Transportation Technologies* 3: 58-67

Bolin CA, Smith S (2013b) Life cycle assessment of creosote-treated wooden rail-road crossties in the US with comparisons to concrete and plastic composite railroad crossties. *Journal of Transportation Technologies* 3: 149-161

Bravery AF (1978) A miniaturised wood-block test for the rapid evaluation of wood preservative fungicides. The International Research Group on Wood Preservation, IRG/WP 2113. IRG Sectretariat, Stockholm, Sweden

Bravery AF, Berry RW, Carey JK, Cooper DE (1987) Recognizing wood rot and insect damage in buildings (1st edition). Building Research Establishment Press

Browne FL (1958) Theories of the combustion of wood and its control. Forest Service Report No. 2136, Forest Products Laboratory, Madison, Wisconsin

Bull DC (2001) The chemistry of chromated copper arsenate II. Preservative-wood interactions. *Wood Science and Technology* 34(6): 459-466

BW (2015) Business Wire. Research and markets: caprolactam (nylon 6 fiber and nylon 6 resin) market - global industry analysis, size, share, growth, trends and forecast 2013-2019. Available from http://www.businesswire.com/news/home/20140218005942/en/Research-Markets-Caprolactam-Nylon-6-Fiber-Nylon#.VRE1reGRNnA

Cai X, Riedl B, Zhang SY, Wan H (2007) Formation and properties of nanocomposites made up from solid aspen wood, melamine-urea-formaldehyde, and clay. *Holzforschung* 61(2): 148-154

Cai X, Riedl B, Zhang SY, Wan H (2008) The impact of the nature of nanofillers on the performance of wood polymer nanocomposites. *Composites Part A: Applied Science and Manufacturing* 39(5): 727-737

Calixto JB, Santos AR, Cechinel Filho V, Yunes RA (1998) A review of the plants of the genus Phyllanthus: their chemistry, pharmacology, and therapeutic potential. *Medicinal Research Reviews* 18(4): 225-258

Camino G, Costa L (1988) Performance and mechanisms of fire retardants in polymers—A review. *Polymer Degradation and Stability* 20(3): 271-294

Camino G, Tartaglione G, Frache A, Manferti C, Costa G (2005) Thermal and combustion behaviour of layered silicate–epoxy nanocomposites. *Polymer Degradation and stability* 90(2): 354-362

Campora CE, Grace JK (2007) Foraging behavior of the Formosan subterranean termite (Isoptera: Rhinotermitidae) in response to borate treated wood. The International Research Group on Wood Preservation, IRG/WP 07-10605. IRG Sectretariat, Stockholm, Sweden

Carr JM, Duggan PJ, Humphrey DG, Tyndall EM (2005) Enhanced anti-fungal activity of the organo-soluble borate ester, tetra-n-butylammonium bis (ortho-hydroxymethylphenolato) borate. *Australian Journal Chemmistry* 58(1): 21-25

Cave ID (1972) A theory of the shrinkage of wood. *Wood Science and Technology* 6(4): 284-292

Cave ID (1997) Theory of X-ray measurement of microfibril angle in wood. *Wood Science and Technology* 31(4): 225-234

ChaichiSemsari M, MaheriSis N, Sadaghian M, Eshratkhah B, Hassanpour S (2011) Effects of administration of industrial tannins on nutrient excretion parameters during naturally acquired mixed nematode infections in Moghani sheep. *Journal of American Science* 7(6): 245-248

Chen GC (2008) Synthesis and evaluation of aminoborates derived from boric acid and diols for protecting wood against fungal and thermal degradation. *Wood and Fiber science* 40(2): 248-257

Chen GC, Ibach RE (2010) Laboratory evaluation of borate/amine/zinc formulations for fungal decay protection. In: *Proceedings, one hundred sixth annual meeting of the American Wood Protection Association*. Savannah, GA. Volume 106, Birmingham, AL: American Wood Protection Association, c2010: pp. 139-145

Chen L, Wang YZ (2010) A review on flame retardant technology in China. Part I: development of flame retardants. *Polymers for Advanced Technologies* 21(1): 1-26

Choudalakis G, Gotsis AD (2009) Permeability of polymer/clay nanocomposites: a review. *European Polymer Journal* 45(4): 967-984

Chow S (1983) Adhesive developments in forest products. *Wood Science and Technology* 17(1): 1-11

Christensen CM, Kaufmann HH (1965) Deterioration of stored grains by fungi. *Annual Review of Phytopathology* 3(1): 69-84

Cockcroft R, Levy JF (1973) Bibliography on the use of boron compounds for the preservation of wood. *Journal Institute of Wood Science* 6(3): 28-37

Čop M, Laborie MP, Pizzi A, Sernek M (2014) Curing characterisation of spruce tannin-based foams using the advanced isoconversional method. *BioResources* 9(3): 4643-4655

Corey EJ (2003) Boron. http://pubs.acs.org/cen/80th/print/boron.html

Cotton FA, Wilkinson G (1988) Boron: Group IIIA(13). Chapter 6, *Advanced Inorganic Chemistry*, 5th Edition. Wiley and Sons. pp. 162-183

Couturier MF, George K, Schneider MH (1996) Thermophysical properties of wood-polymer composites. *Wood Science and Technology* 30(3): 179-196

Crawford RL (1981) Lignin biodegradation and transformation. New York: John Wiley and Sons. ISBN 0-471-05743-6

Cui W, Kamdem P (1999) Bioefficiency of Boric acid grafted on to wood. The International Research Group on Wood Preservation, IRG/WP 99-30202. IRG Secretariat, Stockholm, Sweden

Cullis C F, Hirschler MM (1981) The combustion of organic polymers. Oxford University Press, London, pp. 256-261

Dahlhoff G, Niederer JPM, Hoelderich WF (2001) ε-Caprolactam: new by-product free synthesis routes. *Catalysis Reviews: Science and Engineering* 43(4): 381-441

Deka BK, Maji TK (2011) Effect of TiO_2 and nanoclay on the properties of wood polymer nanocomposite. *Composites Part A: Applied Science and Manufacturing* 42(12): 2117-2125

Deka BK, Maji TK, Mandal M (2011) Study on properties of nanocomposites based on HDPE, LDPE, PP, PVC, wood and clay. *Polymer bulletin*, *67*(9), 1875-1892

Deka M, Saikia CN (2000) Chemical modification of wood with thermosetting resin: effect on dimensional stability and strength property. *Bioresource Technology* 73(2): 179-181

Dirol D, Scalbert A (1991) Improvement of wood decay resistance by tannin impregnation. The International Research Group on Wood Preservation, IRG/WP2380. IRG Secretariat, Stockholm, Sweden

Dotsika E, Poutoukis D, Michelot JL, Kloppmann W (2006) Stable isotope and chloride, boron study for tracing sources of boron contamination in groundwater: boron contents in fresh and thermal water in different areas in Greece. *Water, Air, and Soil Pollution* 174(1-4): 19-32

Drysdale JA (1994) Boron treatments for the preservation of wood: A review of efficacy data for fungi and termites. The International Research Group on Wood Preservation, IRG/WP 94-30037. IRG Secretariat, Stockholm, Sweden

Du-Fresne E, Campbell DL (1967) Method for fireproofing wood and the treated wood. US Patent 3306765

Dunnett N, Clayden A (2007) The raw materials of landscape architecture in landscape and sustainability. 2nd edition edited by Benson, J. & Roe, M. Routledge, London: 196-221

EC (2014) European Commission – Directorate General Joint Research Centre. Institute for Environment and Sustainability. Available from http://eplca.jrc.ec.europa.eu/ResourceDirectory/toolList.vm

Ecoinvent Centre (2013) Ecoinvent data v3.0. Swiss Centre for Life Cycle Inventories, St. Gallen, retrieved from: www.ecoinvent.org

EN 117 (2013) Wood Preservatives-Determination of Toxic Values against Reticulitermes Species (European Termites) (Laboratory method)

EN 118 (2014) Wood preservatives-Determination of preventive action against Reticulitermes species (European termites) (Laboratory method)

EN 1534 (2000) Wood and parquet flooring - determination of resistance to indentation (Brinell) - test method

EN 335 (2013) Durability of wood and wood-based products – Use classes: definitions, application to solid wood and wood-based products, European Committee for Standardization

EN 350-1 (1994) Durability of Wood and Wood-based Products – Natural Durability of Solid Wood: Guide to the principles of testing and classification of the natural durability of wood, European Committee for Standardization

EN 350-2 (1994) Durability ofWood andWood-based Products–Natural Durability ofSolid Wood Part 2: Guide to Natural Durability and Treatability of SelectedWood Species of Importance for Europe

EN 84 (1997) Wood Preservatives.Accelerated Ageing of Treated Prior to BiologicalTesting. Leaching Procedure

EN 927-6 (2006) European standard. Paints and varnishes – Coating materials and coating systems for exterior wood. Part 6: Exposure of wood coatings to artificial weathering using fluorescent UV and water

EN113 (1996) Wood preservatives. Method for determining the protectiveeffectiveness against wood destroying basidiomycetes. Determination of toxic values

EN 14080 (2013) Timber structures. Glued laminated timber and glued solid timber. Requirements

Engler N (2009) Nick Engler's Workshop Companion. Available from http://workshopcompanion.com/KnowHow/Wood/Hardwoods_&_Softwoods/1_Wood_Botany/1_Wood_Botany.htm

ENV 1250-2 (1995) Wood preservatives—methods for measuringlosses of active ingredients and other preservative ingredientsfrom treated timber—part 2: laboratorymethod for obtaining samplesfor analysis tomeasure losses by leaching into water or syntheticsea water

ENV 807 (2001) Wood preservatives. Determination of the effectiveness against soft rotting micro-fungi and other soil inhabiting micro-organisms

Erdem P, Bursali EA, Yurdakoc M (2013) Preparation and characterization of tannic acid resin: Study of boron adsorption. *Environmental Progress and Sustainable Energy 32*(4): 1036-1044

Erel-Unal I, Sukhishvili SA (2008) Hydrogen-bonded hybrid multilayers: film architecture controls release of macromolecules. *Macromolecules* 41(22): 8737-8744

Eriksson KEL, Blanchette RA, Ander P (1990) Microbial and enzymatic degradation of wood and wood components. Berlin: Springer-verlag

Eriksson Ö, Goring D AI, Lindgren BO (1980) Structural studies on the chemical bonds between lignins and carbohydrates in spruce wood. *Wood Science and Technology* 14(4): 267-279

Erlandsson M, Oedeen K, Eddlund ML (1992) Environmental consequences of various materials in utility poles - A Life Cycle Analysis. The International Research Group on Wood Preservation, IRG/WP 3726-92. IRG Secretariat, Stockholm, Sweden

ES (2011) EarthShift. SimaPro LCA software-The LCA expert's tool of choice. LCA software for measuring sustainability impact. Available from http://www.earthshift.com/software/simapro

Evans P (2003) Emerging technologies in wood protection. *Forest Products Journal* 53(1): 14-22

Ezechi EH, Isa MH, Kutty SR, Sapari NB (2011) Boron recovery, application and economic significance: a review. In *National Postgraduate Conference (NPC)*, IEEE 1-6

Falck R, Ketkar V (1934) Prufung und schutzwerbestimmung der feuerschutzmittel des holzes. Hausschwammforschungen, *Jena (G. Fischer)*, 1, Heft, 46

Farber E (1951) Process for producing cupric ammonium borate solutions. US Patent 2573253

Fava J, Denison R, Jones B, Curran M, Vigon B, Selke S, Barnum J (1991) A technical framework for life-cycle assessment. Pensacola (FL): SETAC Press

Fechtal M, Riedl B (1993) Use of eucalyptus and *Acacia mollissima* bark extract -formaldehyde adhesives in particleboard manufacture. *Holzforschung* 47: 349-357

Feist WC (1983) Weathering and protection of wood. *Product American Wood Preserver's Association* 79: 195-205

Finon D, Romano E (2009) Electricity market integration: Redistribution effect versus resource reallocation. Energy Policy, 37(8): 2977-2985

Fradinho DM, Neto CP, Evtuguin D, Jorge FC, Irle MA, Gil MH, De Jesus JP (2002) Chemical characterisation of bark and of alkaline bark extracts from maritime pine grown in Portugal. *Industrial Crops and Products* 16(1): 23-32

Freeman M, Mc Intyre C, Jackson D (2009)A critical and comprehensive review of boron in wood preservation. Proceedings of the annual meeting of AWPA, 105, 16

Freeman MH, Amburgey TL (1997) Groundline treatments with a water borne copper naphthenate-boron paste. In: Proceedings Second International Conference on Wood Protection with Diffusible Preservatives and Pesticides. Mobile AL. Proceedings No. 7284. Forest Product Society, Madison, WI. pp.186

Freeman MH, McIntyre CR, Jackson RE (2009) A critical and comprehensive review of boron in wood preservation. In Proceedings of the American Wood Protection Association. Birmingham, AL.

Frischknecht R, Jungbluth N, Althaus HJ, Bauer C, Doka G, Dones R, Hischier R, Hellweg S, Humbert S, Köllner T, Loerincik Y, Margni M, Nemecek T (2007) Implementation of life cycle impact assessment methods. Ecoinvent report No. 3, Data v2.0. Swiss Centre for Life Cycle Inventories, Düebendorf (Switzerland)

Frischknecht R, Jungbluth N, Althaus HJ, Bauer C, Doka G, Dones R, Hischier R, Hellweg S, Humbert S, Köllner T, Loerincik Y, Margni M, Nemecek T (2007) Implementation of life cycle impact assessment methods. data v2.0, Ecoinvent report No. 3, Ecoinvent Centre, Swiss Federal Laboratories for Materials Testing and Research (EMPA), Dübendorf (Switzerland)

Funatogawa K, Hayashi S, Shimomura H, Yoshida T, Hatano T, Ito H, Hirai Y (2004) Antibacterial activity of hydrolyzable tannins derived from medicinal plants against Helicobacter pylori. *Microbiology and Immunology* 48(4): 251-261

Furuno T, Fuyuki W, Yusuf S (2006) Biological resistance of wood treated with zinc and copper metaborates. *Holzforschung* 60(1): 104-109

Furuno T, Lin L, Katoh S (2003) Leachability, decay, and termite resistance of wood treated with metaborates. *Wood Science and Technology* 49(4): 344-348

Gauntt JC, Amburgey TL (2005) Decay in wood ties……..Problem solved! The American Railway Engineering and Maintenance of Way Association (AREMA) manuscript

Gentz MC, Grace JK (2009) The response and recovery of the formosan subterranean termite (Coptotermes formosanus Shiraki) from sublethal boron exposures. *International Journal of Pest Management* 55(1): 63-67

Giniyatullina YR, Peresypkina EV, Virovets AV, Cherkasova TG, Tatarinova ES (2015) Synthesis, physicochemical properties, and structural isomerism of cadmium chloride coordination compounds with ε-caprolactam. *Russian Journal of Inorganic Chemistry* 60(1): 46-50

Goedkoop M, Heijungs R, Huijbregts M, De Schryver A, Struijs J, van Zelm R (2009) ReCiPe 2008: A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level (Report I: Characterisation), Ministerie van VROM Rijnstraat 8, 2515 XP Den Haag, www.vrom.nl

Goedkoop M, Oele M, Leijting J, Ponsioen T, Meijer E (2013) SimaPro 7- Introduction to LCA with SimaPro 7, PRé Consultants, The netherlands

Goldblatt MW, Farquharson ME, Bennett G, Askew BM (1954) ε-Caprolactam. *British journal of Industrial Medicine* 11(1): 1

Gorrasi G, Tortora M, Vittoria V, Galli G, Chiellini E (2002) Transport and mechanical properties of blends of poly (ε-caprolactone) and a modified montmorillonite–poly(ε-caprolactone) nanocomposite. *Journal of Polymer Science, Part B: Polymer Physics* 40 (11): 1118-1124

Grace JK (1997) Review of recent research on the use of borates for termite prevention. In Proceedings of the 2nd International Conference on Wood Protection with Diffusible Preservatives and Pesticides. Forest Products Society, Madison, WI pp. 85-92

Grace JK, Yamamoto RT (1993) Sequential exposure of borate treated Douglas-fir to multiple Formosan subterranean termite colonies in a 40-week field test. The International Research Group on Wood Preservation, IRG/WP 93-10006. IRG Secretariat, Stockholm, Sweden

Grace JK, Yamamoto RT, Tamashiro M (1992) Resistance of borate-treated Douglas-fir to the Formosan subterranean termite. *Forest Products Journal* 42(2): 61-65

Greene-Kelly R (1957) The montmorillonite minerals, in: R.C. Mackenzie (Ed.). The differential thermal investigation of clays, Mineralogical Society, London. pp. 140

Guinee JB, Heijungs R, Huppes G, Zamagni A, Masoni P, Buonamici R, Ekvall T, Rydberg T (2011) Life cycle assessment: past, present, and future. *Environmental Science and Technology* 45(1): 90-96

Gupta A, Singhal R, Nagpal AK (2005) Reactive blends of epoxy resin (DGEBA) crosslinked by anionically polymerized polycaprolactam. II. Mechanical and electrical properties. *Journal of Applied Polymer Science* 96(2): 537-549

GWQS (2002) Ground water quality standard for caprolactam (CASRN# 105-60-2). New Jersey Department of Environmental Protection. Division of Water Monitoring and Standards-Bureau of Water Quality Standards and Assessment.

Hagerman AE, Riedl KM, Jones GA, Sovik KN, Ritchard NT, Hartzfeld PW, Riechel TL (1998) High molecular weight plant polyphenolics (tannins) as biological antioxidants. *Journal of Agricultural and Food Chemistry* 46(5): 1887-1892

Hansmann C, Deka M, Wimmer R, Gindl W (2006) Artificial weathering of wood surfaces modified by melamine formaldehyde resins. *HolzalsRoh-und werkstoff* 64(3): 198-203

Haslam E (1986) Hydroxybenzoic acids and the enigma of gallic acid. In *The Shikimic Acid Pathway*, Springer US. pp. 163-200

Hassanpour S, MaheriSis N, Eshratkhah B (2011) Plants and secondary metabolites (Tannins): A Review. *International Journal of Forest, Soil and Erosion (IJFSE)* 1(1): 47-53

Hassanpour S, Sadaghian M, MaheriSis N, Eshratkhah B, ChaichiSemsari M (2011) Effect of condensed tannin on controlling faecal protein excretion in nematode-infected sheep: in vivo study. *Journal of American Science* 7(5): 896-900

Häussermann U, Mikhaylushkin AS (2010) Structure and bonding of γ-B_{28}: Is the high pressure form of elemental boron ionic? *Inorganic Chemistry* 49(24): 11270-11275

Hazarika A, Maji TK (2013) Study on the properties of wood polymer nanocomposites based on melamine formaldehyde-furfuryl alcohol copolymer and modified clay. *Journal of Wood Chemistry and Technology* 33(2): 103-124

Hedley CB, Yuan G, Theng B (2007) Thermal analysis of montmorillonites modified with quaternary phosphonium and ammonium surfactants. *Applied Clay Science* 35(3): 180-188

Hedley M, Page D (2006) Performance of boron treated radiata pine in above ground field tests in New Zealand. The International Research Group on Wood Protection, IRG/WP 06-30406. IRG Secretariat, Stockholm, Sweden

Hedley M, Page D, Patterson B (2000) Performance of Tebbacop in laboratory, fungus cellar and field tests. The International Research Group on Wood Preservation, IRG/WP 00-30222. IRG Secretariat, Stockholm, Sweden

Hillier W, Murphy RJ, Dickinson DJ, Bell JNB (1995) LCA examination of preservative treated timber products and alternatives; initial results. Proceedings of the 3rd. Int. Wood Preservation Symp. The Challenge – Safety and Environment. Cannes, 58-69

Hillis WE (1971) Distribution, properties and formation of some wood extractives. *Wood Science and Technology* 5(4): 272-289

Homan WJ, Militz H (1995) Influence of surface coating on the leachability of boric acid and bifluorides from spruce wood. The International Research Group on Wood Preservation, IRG/WP 95-50050. IRG Secretariat, Stockholm, Sweden

Hoong YB, Paridah MT, Loh YF, Jalaluddin H, Chuah LA (2011) A new source of natural adhesive: Acacia mangium bark extracts co-polymerized with phenol-formaldehyde (PF) for bonding Mempisang (Annonaceae spp.) veneers. *International Journal of Adhesion and Adhesives* 31(3): 164-167

Hopkinson L, James P, Lenegan N, McGrath T, Tait M (2011) Energy Consumption of University Laboratories: Detailed Results from S-Lab Audits. www.goodcampus.org, 47.

Humphrey CJ, Siggers PV (1933) Temperature relations of wood-destroying fungi. *Journal of Agricultural Research* 47(12): 947-1008

Humphrey DG, Duggan PJ, Tyndall EM, Carr JM, Cookson LJ (2002) New boron based biocides for the protection of wood. The International Research Group on Wood Preservation, IRG/WP 02-30283. IRG Secretariat, Stockholm, Sweden

Hunt CD (2012) Dietary boron: progress in establishing essential roles in human physiology. *Journal of Trace Elements in Medicine and Biology* 26(2-3): 157-160

Hunt RG, Franklin WE, Hunt RG (1996) LCA—How it came about. *The International Journal of Life Cycle Assessment* 1(1): 4-7

Huskić M, Brnardić I, Žigon M, Ivanković M (2008) Modification of montmorillonite by quaternary polyesters. *Journal of Non-Crystalline Solids* 354(28): 3326-3331

Hussain F, Hojjati M, Okamoto M, Gorga RE (2006) Review article: polymer-matrix nanocomposites, processing, manufacturing, and application: an overview. *Journal of Composite Materials* 40(17): 1511-1575

Hutter FG, Lake MA, Smith DL, Robinson PH, Bishop FE (2004) Method for treating wood. US Patent 2194827

Hyakutake M, Sonoda M, Katase A, Wakuta Y, Matoba M, Tawara H, Fujita I (1974) Scattering of 14.1 MeV Neutrons by ^{6}Li, ^{7}Li, ^{9}Be, ^{10}B and ^{11}B. *Journal of Nuclear Science and Technology* 11(10): 407-421

IBM (2014) Indian Bureau of Mines. Indian Minerals Yearbook 2012, Part-III: Mineral reviews. 51st Edition. Boron Minerals (Final Release). Government of India, Ministry of Mines: 1-7

ISO (2006a) ISO 14040: Environmental management - Life cycle assessment - Principles and framework. International Organization for Standardization, Geneva, Switzerland

ISO (2006b) ISO 14044**:** Environmental management- Life cycle assessment - Requirements and guidelines. International Organization for Standardization, Geneva, Switzerland

Iversen T (1985) Lignin-carbohydrate bonds in a lignin-carbohydrate complex isolated from spruce. *Wood Science and Technology* 19(3): 243-251

Iversen T, Westermark U, Samuelsson B (1987) Some components on the isolation of galactose-containing lignin-carbohydrate complexes. *Holzforschung* 41: 119-121

Ivković M, Gapare WJ, Abarquez A, Ilic J, Powell MB, Wu HX (2009) Prediction of wood stiffness, strength, and shrinkage in juvenile wood of radiata pine. *Wood Science and Technology* 43(3-4): 237-257

Jorge FC, Nunes L, Botelho C (2004) Boron in wood preservation: problems, challenges and proposed solutions: an overview on recent research. *Journal of the Faculty Science Technology (University Fernando Pessoa)* 1: 3-15

Kabu M, Akosman MS (2013) Biological effects of boron. In *Reviews of Environmental Contamination and Toxicology*. Whitacre DM (Ed.), Springer Science+Business Media New York 57-75

Kabu M, Civelek T (2012) Effects of propylene glycol, methionine and sodium borate on metabolic profile in dairy cattle during periparturient period. *Revue de Medecine Veterinaire* 163(8-9): 419-430

Kandola BK, Horrocks AR (1996) Flame-retardant treatments of cellulose and their influence on the mechanism of cellulose pyrolysis. *Journal of Macromolecular Science, Part C: Polymer Reviews* 36(4):721-794

Kaps T, Reiska R, Kallavus U, Koolme M, Luga Ü, Kers J (2012) Effective protection of pinewood against fungal attack. *Agronomy Research* 10(Special Issue I): 123-129

Kar Y, Şen N, Demİrbaş A (2006) Boron minerals in Turkey, their application areas and importance for the country's economy. *Minerals and Energy-Raw Materials Report* 20(3-4): 2-10

Kartal NS, Green F (2003) Leachability of boron from wood treated with natural and semi-synthetic polymers and calcium precipitating agent. *Holz als Roh und Werkstoff* 61: 388-389

Kartal NS, Imamura Y (2003) Leaching characteristics, decay and termite resistance of treated wood with boron compounds, N'-N-(1, 8-Naphthalyl) hydroxylamine (NHA-Na), and hydroxynaphthalimide (NHA-H). The International Research Group on Wood Preservation, IRG/WP 03-30351. IRG Secretariat, Stockholm, Sweden

Kartal S N, Shinoda K, Imamura Y (2005) Laboratory evaluation of boron-containing quaternary ammonia compound, didecyl dimethyl ammonium tetrafluoroborate (DBF) for inhibition of mold and stain fungi. *Holz als Roh-und Werkstoff* 63(1): 73-77

Kartal SN, Hwang WJ, Shinoda K, Imamura Y (2006) Laboratory evaluation of boron-containing quaternary ammonia compound, didecyl dimethyl ammonium tetrafluoroborate (DBF) for control of decay and termite attack and fungal staining of wood. *Holz als Roh-und Werkstoff* 64(1): 62-67

Kartal SN, Yoshimura T, Imamura Y (2009) Modification of wood with Si compounds to limit boron leaching from treated wood and to increase termite and decay resistance. *International Biodeterioration and Biodegradation* 63(2): 187-190

Kazunobu S (1995) Wood preservative composition, process for treating wood with the same, wood treated with the same. US Patent 5478598

Khanbabaee K, van Ree T (2001) Tannins: classification and definition. *Natural Product Reports* 18(6): 641-649

Kharlampieva E, Kozlovskaya V, Tyutina J, Sukhishvili SA (2005) Hydrogen-bonded multilayers of thermoresponsive polymers. *Macromolecules* 38(25): 10523-10531

Kirker G, Winandy J (2014) Above ground deterioration of wood and wood-based materials. In *Deterioration and protection of sustainable biomaterials*. Nicholas D, Goodell B, Schultz T (Eds.) ACS Symposium Series, Wash.DC. Chapter 6: 113-129

Kistler RB, Helvaci C (1994) Boron and borates. *Industrial Minerals and Rocks* 6: 171-186

Kloppenburg AG, Esser PM (1994) Environmental life cycle analysis of reusable wood and plastic pallets. TNO Report 94.10131

Kochkodan V, Darwish NB, Hilal N (2015) The chemistry of boron in water. In *Boron Separation Processes*. Kabay N, Bryjak M, Hilal N (Ed.) Elsevier, pp.37

Kollmann FFP (1968) Mechanics and rheology of wood. Principles of wood science and technology I: solid wood. Springer, Berlin, pp. 292-419

Kord B, Hemmasi AH, Ghasemi I (2011) Properties of PP/wood flour/organomodified montmorillonite nanocomposites. *Wood Science and Technology* 45(1): 111-119

Kornmann X, Lindberg H, Berglund LA (2001) Synthesis of epoxy–clay nanocomposites: influence of the nature of the clay on structure. *Polymer* 42(4): 1303-1310

Köse C, Terzi E, Kartal SN, Erilkun B, Imamura Y (2013) Preliminary evaluation of boron release and biological resistance of wood treated with disodium octoborate tetrahydrate (DOT) and a water-repellent compound. *African Journal of Biotechnology* 10(10): 1833-1839

Kuenniger T, Richter K (1995) Life cycle analysis of utility poles: A Swiss case study. The International Research Group on Wood Preservation, IRG/WP 95-50010. IRG Secretariat, Stockholm, Sweden

Kumar AP, Singh RP (2007) Novel hybrid of clay, cellulose, and thermoplastics. I. Preparation and characterization of composites of ethylene–propylene copolymer. *Journal of Applied Polymer Science* 104(4): 2672-2682

Kurakevych OO, Le Godec Y, Hammouda T, Goujon C (2012) Comparison of solid-state crystallization of boron polymorphs at ambient and high pressures. *High Pressure Research* 32(1): 30-38

Lacoste C, Basso MC, Pizzi A, Laborie MP, Celzard A, Fierro V (2013) Pine tannin-based rigid foams: mechanical and thermal properties. *Industrial Crops and Products* 43: 245-250

Lacoste C, Pizzi A, Basso MC, Laborie MP, Celzard A (2014) Pinus pinaster tannin/furanic foams: PART I. Formulation. *Industrial Crops and Products* 52: 450-456

Lagaly G (1986) Interaction of alkylamines with different types of layered compounds. *Solid State Ionics* 22(1): 43-51

Lagaly G (1994) Layer charge determination by alkylammoniumions. In: Mermut AR, editor. Layer charge characteristicsof 2:1 silicate clay minerals.CMS WorkshopLectures, vol. 6. Boulder, CO: Clay Miner Soc. pp1-46

Lake MA, McIntyre CR (2006) Formosan termite response to weathered borate-treated wood. In *Wood Protection 2006*, Session VI, Forest Product Society, Madison, Wisconsin, US. pp. 295-298

Laks PE, Manning MJ (1994) Inorganic borates as preservative systems for wood composites. In: Proceedings of the 2nd Pacific Rim bio-based composites symposium. Vancouver, B.C. Canada. pp. 236-244

Laks PE, McKaig PA, Hemingway RW (1988) Flavonoid biocides: wood preservatives based on condensed tannins. *Holzforschung* 42(5): 299-306

Lan T, Kaviratna PD, Pinnavaia TJ (1995) Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites. *Chemistry of Materials* 7(11): 2144-2150

Laubengayer AW, Hurd DT, Newkirk AE, Hoard JL (1943) Boron. I. Preparation and properties of pure crystalline boron. *Journal of the American Chemical Society* 65(10): 1924-1931

LeBaron PC, Wang Z, Pinnavaia TJ (1999) Polymer-layered silicate nanocomposites: an overview. *Applied Clay Science* 15(1): 11-29

Lee H, Kim DS (2009) Preparation and physical properties of wood/polypropylene/clay nanocomposites. *Journal of Applied Polymer Science* 111(6): 2769-2776

Lee SY, Kang IA, Doh GH, Kim WJ, Kim JS, Yoon HG, Wu Q (2008) Thermal, mechanical and morphological properties of polypropylene/clay/wood flour nanocomposites. *Express Polymer Letters* 2(2): 78-87

Lei H, Pizzi A, Du G (2008) Environmentally friendly mixed tannin/lignin wood resins. *Journal of Applied Polymer Science* 107(1): 203-209

Lei Y, Wu Q, Clemons CM (2007) Preparation and properties of recycled HDPE/clay hybrids. *Journal of Applied Polymer Science* 103(5): 3056-3063

Lesar B, Humar M (2009) Re-evaluation of fungicidal properties of boric acid. *European Journal of Wood and Wood Products* 67(4): 483-484

Lesar B, Humar M, Kralj P (2010) Influence of montan wax emulsions on leaching dynamics of boric acid from impregnated wood. *Wood Research* 55(1): 93-100

Lesar B, Kralj P, Humar M (2009) Montan wax improves performance of boron-based wood preservatives. *International Biodeterioration and Biodegradation* 63(3): 306-310

Lesar B, Podlesnik B, Pohleven F, Humar M, Kralj P, Veber M (2008) Performance of boron ethanolamine quaternary ammonium based wood preservatives against leaching, wood decay and blue stain fungi. *Wood Research* 53(3): 17-26

LeVan S (1984) Chemistry of fire retardancy. In *The Chemistry of Solid Wood* Rowell RM (Ed.) Advances in Chemistry Series 207, Ch. 14, American Chemical society, Washington, D.C. PP. 531-574

LeVan SL, Tran HC (1990) The role of boron in flame-retardant treatments. In: *Proceedings of the 1st International Conference on Wood Protection with Diffusible Preservatives.* Nashville, TN. Madison, WI, Forest Products Research Society pp. 39-41

Li J, Maplesden F (1998) Commercial production of tannins from radiata pine bark for wood adhesives. Transactions of the Institution of Professional Engineers New Zealand: Electrical/Mechanical/Chemical Engineering Section, 25(1): 46-52

Li X, Nicollin A, Pizzi A, Zhou X, Sauget A, Delmotte L (2013) Natural tannin-furanic thermosetting moulding plastics. *RSC Advances* 3(39): 17732-17740

Li X, Pizzi A, Fierro V, Alain A (2014) Formaldehyde-free prorobitenidin/profisetinidin tannin/furanic foams based on alternative aldehydes: glyoxal and glutaraldehyde. *Journal of Renewable Materials* http://dx.doi.org/10.7569/JRM.2014.634117

Liese W, Bauch J (1967) On the closure of bordered pits in conifers. *Wood Science and Technology* 1(1): 1-13

Lin L, Furuno T, Katoh S (2001) Leachability and decay resistance of tetraphenylborate salt-treated wood. *Holzforschung* 55(4): 355-357

Liu R, Cao J, Xu W, Li H (2012) Study on the anti-leaching property of Chinese fir treated with borate modified by phenol-formaldehyde resin. *Wood Research* 57(1): 111-120

Liu X, Laks PE, Pruner MS (1994) A preliminary report on the wood preservative properties of phenyl boronic acid. *Forest Products Journal* 44(6): 46-48

Liu YG, Ren YL, Dong EY (2011) Development of environmental friendly flame retardants for wood plastic composites (WPC). *Advanced Materials Research* 332: 1880-1883

Lloyd JD (1993) The mechanisms of action boron-containing wood preservatives. Ph.D. Thesis, University of London, London, pp.34-35

Lloyd JD (1998) Borates and their biological applications. The International Research Group on Wood Preservation, IRG/WP 98-30178. IRG Secretariat, Stockholm, Sweden

Lloyd JD, Fogel JL (2005) Wood preservative concentrate. US Patent 6896908

Lloyd JD, Fogel JL, Vizel A (2001) The use of Zirconium as an inert fixative for borates in Preservation. The International Research Group on Wood Preservation, IRG/WP 01-30256. IRG Secretariat, Stockholm, Sweden

Long R (1991) Quebracho based polyphenols for use in wood panel adhesive system. *Holz Roh-Werkstoff* 49: 485-487

Lotz WL, Hollaway DF (1988) Wood preservation. US Patent Number 4732817

Lyon F, Thevenon MF, Hwang WJ, Imamura Y, Gril J, Pizzi A (2007) Effect of an oil heat treatment on the leachability and biological resistance of boric acid impregnated wood. *Annals of forest science*, *64*(6), 673-678.

Madejova J (2003) FTIR techniques in clay mineral studies. *Vibrational Spectroscopy* 31(1): 1-10

Malça J, Freire F (2006) Renewability and life-cycle energy efficiency of bioethanol and bio-ethyl tertiary butyl ether (bioETBE): Assessing the implications of allocation. Energy, 31(15): 3362-3380

Malouf GM, Docks EL (1991) Aqueous boron–containing compositions. US Patent 5061698

Mansouri HR, Navarrete P, Pizzi A, Tapin-lingua S, Benjelloun-Mlayah B, Pasch H, Rigolet S (2010) Synthetic-free wood panel adhesives from mixed low molecular mass lignin and tannin. *European Journal of Wood and Wood Products* 69(2): 221–229

Mascal M (2012) Chemicals from biobutanol: technologies and markets. *Biofuels, Bioproducts and Biorefining* 6(4): 483-493

Masson E, Pizzi A, Merlin A (1996) Comparative kinetics of the induced radical autocondensation of polyflavonoid tannins. III. Micellar reactions vs. cellulose surface catalysis. *Journal of Applied Polymer Science* 60(10): 1655-1664

Mastromatteo E, Sullivan F (1994) Summary: International symposium on the health effects of boron and its compounds. *Environmental Health Perspectives* 102(Suppl 7): 139-141

Maynard NP (1993) Method of preparing a borate organic complex anion containing salt composition. US Patent 5221758

McNally T, Murphy WR, Lew CY, Turner RJ, Brennan GP (2003) Polyamide-12 layered silicate nanocomposites by melt blending. *Polymer* 44(9): 2761-2772

Mehrotra V, Giannelis EP (1989) Conducting molecular multilayers: intercalation of conjugated polymers in layered media. In *MRS Proceedings*. Cambridge University Press. Vol. 171, pp. 39

Meikleham N, Pizzi A, Stephanou A (1994) Induced accelerated autocondensation of polyflavonoid tannins for phenolic polycondensates. I. 13C ‐ NMR, 29Si ‐ NMR, X ‐ ray, and polarimetry studies and mechanism. *Journal of Applied Polymer Science* 54(12): 1827-1845

Menzies, RJ (1957) The marine borer family Limnoriidae (Crustacea, Isopoda). Part I: Northern and central America: systematics, distribution, and ecology. *Bulletin of Marine Science*, *7*(2): 101-200.

MFS (2015) Mihilaka Forestry Service. Treatment process and wood preservation process. In Wood Preservation. Available from http://www.timber.lk/PRASERVATION/Wood-preservation-process/index.html

Mittal V (2009) Polymer layered silicate nanocomposites: a review. *Materials* 2(3): 992-1057

Miyafuji H, Saka S (2001) Na_2O-SiO_2 wood-inorganic composites prepared by the sol-gel process and their fire-resistant properties. *Journal of Wood Science* 47(6) :483-489

Mohareb A, Thévenon MF, Wozniak E, Gérardin P (2011) Effects of polyvinyl alcohol on leachability and efficacy of boron wood preservatives against fungal decay and termite attack. *Wood Science and Technology* 45(3): 407-417

Mohareb A, Van Acker J, Stevens M (2002) Effect of additives on the leachability and efficacy of borate treated wood. The International Research Group on Wood Preservation, IRG/WP 02-30290. IRG Secretariat, Stockholm, Sweden

Morris PI, Grace JK, Yoshimura T, Tsunoda K (2014) An international termite field test of wood treated with insecticides in a buffered amine oxide carrier. *Forest Products Journal* 64(5/6): 156-160

Mourant D, Yang DQ, Lu X, Riedl B, Roy C (2009) Copper and boron fixation in wood by pyrolytic resins. *Bioresource Technology* 100(3): 1442-1449

Müller U, Rätzsch M, Schwanninger M, Steiner M, Zöbl H (2003a) Yellowing and IR-changes of spruce wood as result of UV-irradiation. *Journal of Photochemistry and Photobiology B: Biology* 69 (2): 97-105

Müller U, Rätzsch M, Schwanninger M, Steiner M, Zöbl H (2003b) Accelerated weathering test for evaluation of wood preservative efficacy. The International Research Group on Wood Preservation, IRG/W 03-20262. IRG Secretariat, Stockholm, Sweden

Müller-Hagedorn M, Bockhorn H, Krebs L, Müller U (2003) A comparative kinetic study on the pyrolysis of three different wood species. *Journal of analytical and Applied Pyrolysis* 68: 231-249

Murphy RJ, Turner P (1989) A vapour phase preservative treatment of manufactured wood based board materials. *Wood Science and Technology* 23(3): 273-279

Nakayama FS, Vinyard SH, Chow P, Bajwa DS, Youngquist JA, Muehl JH, Krzysik AM (2001) Guayule as a wood preservative. *Industrial Crops and Products* 14(2): 105-111

Nasheri K (1999) Liquid boron preservative process. U.S. Patent No. 5,871,817. Washington, DC: U.S. Patent and Trademark Office.

NF B 50-003 (1985) Bois Vocabulaire

Nicollin A, Li X, Girods P, Pizzi A, Rogaume Y (2013) Fast pressing composite using tannin-furfuryl alcohol resin and vegetal fibers reinforcement. *Journal of Renewable Materials* 1(4): 311-316

Nielsen FH (1997) Boron in human and animal nutrition. *Plant and Soil* 193(1-2): 199-208

Nies NP, Hulbert RW (1967) Solubility isotherms in the system sodium oxide-boric oxide-water. Revised solubility-temperature curves of boric acid, borax, sodium pentaborate, and sodium metaborate. *Journal of Chemical and Engineering Data* 12(3): 303-313

NPI (2014) National Pollutant Inventory. Boron and compounds. Available from http://www.npi.gov.au/resource/boron-and-compounds

Nzokou P, Wehner K, Kamdem DP (2005) Natural durability of eight tropical hardwoods from Cameroon. *Journal of Tropical Forest Science* 17(3): 416-427

Obanda DN, Shupe TF, Barnes HM (2008) Reducing leaching of boron-based wood preservatives–A review of research. *Bioresource Technology* 99(15): 7312-7322

O'Connor K, Pocock C, Barthelmeh M, Davis S (2011) Carbon and environmental profiling of hard landscape materials. Land Environment and People research report, Lincoln University, LEaP, Canterbury, (22):5-7

Oganov AR, Solozhenko VL (2009) Boron: a hunt for superhard polymorphs. *Journal of Superhard Materials* 31(5): 285-291

Ollier C (1984) Weathering (No. Second edition). Longman Group

Ouchiyama N, Zhang Y, Omori T, Kodama T (1993) Biodegradation of Carbazole by Pseudomonas spp. CA06 and CA10, *Bioscience, Biotechnology and Biochemistry* 57(3): 455-460

Ozaki SK, Yalinlilic MK, Imamura Y, Souza MF (2001) Effect of boron compounds-furfuryl alcohol treatment of wood on dimensional stability, termite resistance and boron leachability. The International Research Group on Wood Preservation, IRG/WP 01-40195. IRG Secretariat, Stockholm, Sweden

Palanti S, Feci E, Predieri G, Vignali F (2012) A wood treatment based on siloxanes and boric acid against fungal decay and coleopter *Hylotrupes bajulus*. *International Biodeterioration and Biodegradation* 75: 49-54

Pan M, Mei C, Du J, Li G (2014) Synergistic effect of nano silicon dioxide and ammonium polyphosphate on flame retardancy of wood fiber-polyethylene composites. *Composites Part A: Applied Science and Manufacturing* 66: 128-134

Pang S (2002) Predicting anisotropic shrinkage of softwood Part 1: Theories. *Wood Science and Technology 36*(1): 75-91

Pavlidou S, Papaspyrides CD (2008) A review on polymer–layered silicate nanocomposites. *Progress in Polymer Science* 33(12): 1119-1198

Pena C, De la Caba K, Retegi A, Ocando C, Labidi J, Echeverria JM, Mondragon I (2009) Mimosa and chestnut tannin extracts reacted with hexamine in solution. *Journal of Thermal Analysis and Calorimetry* 96(2): 515-521

Pennington DW, Potting J, Finnveden G, Lindeijer E, Jolliet O, Rydberg T, Rebitzer G (2004) Life cycle assessment Part 2: Current impact assessment practice. *Environment International* 30(5): 721-739

Petersen AK, Solberg B (2003) Substitution between floor constructions in wood and natural stone: comparison of energy consumption, greenhouse gas emissions, and costs over the life cycle. *Canadian Journal of Forest Research* 33(6): 1061-1075

Pettersen RC (1984) The chemical composition of wood. *The Chemistry of Solid Wood* 207: 57-126

Peylo A, Willeitner H (1995a) The problem of reducing the leachability of boron by water repellents. *Holzforschung* 49(3): 211-216

Peylo A, Willeitner H (1995b) Influence of hydrophobic agents on the leachability of boron. The International Research Group on Wood Preservation, IRG/WP/95-30064. IRG Secretariat, Stockholm, Sweden

Pichelin F, Kamoun C, Pizzi A (1999) Hexamine hardener behaviour: effects on wood gluing, tannin and other wood adhesives. *Holz Roh Werkst* 57(5): 305-317

Pizzi A (1977) Hot-setting tannin–urea–formaldehyde exterior wood adhesives. *Adhesives age* 20(12): 27-29

Pizzi A (1980) Tannin-based adhesives. *Journal of Macromolecular Science—Reviews in Macromolecular Chemistry* 18(2): 247-315

Pizzi A (1982) Condensed tannins for adhesives. *Industrial and Engineering Chemistry Product Research and Development* 21(3): 359-369

Pizzi A (1983) Wood Adhesives: Chemistry and Technology. New York: Dekker.

Pizzi A (2015) Wood products and green chemistry. *Annals of Forest Science*, DOI 10.1007/s13595-014-0448-3

Pizzi A, Baecker A (1996) A new boron fixation mechanism for environment friendly wood preservatives. *Holzfurschung* 50(6): 507-510

Pizzi A, Kueny R, Lecoanet F, Massetau B, Carpentier D, Krebs A, Ragoubi M (2009) High resin content natural matrix–natural fibre biocomposites. *Industrial Crops and Products* 30(2): 235-240

Pizzi A, Meikleham N (1995) Induced accelerated autocondensation of polyflavonoid tannins for phenolic polycondensates. Part 3. *Journal of Applied Polymer Science* 55: 1265-1269

Pizzi A, Meikleham N, Stephanou A (1995) Induced accelerated autocondensation of polyflavonoid tannins for phenolicpolycondensates. Part 2. *Journal of Applied Polymer Science* 55: 929-933

Pizzi A, Orovan E, Singmin M, Jansen A, Vogel MC (1984) Experimental variations in the distribution of CCA preservative in lignin and holocellulose as a function of treating conditions (temperature, concentration, pH, species, and time). *Holzforschung und Holzverwertung* 36(4): 67-77

Pizzi A, Scharfetter H, Kes EW (1981) Adhesives and techniques open new possibilities for the wood processing industry. *Holz als Roh-und Werkstoff* 39(3): 85-89

Pizzi A, Stracke P, Trosa A (1997) Industrial tannin/hexamine low-emission exterior particleboards. *European Journal of Wood and Wood Products* 55(2): 168-168

Pizzi A, Tekely P (1995) Mechanism of polyphenolic tannin resin hardening by hexamethylenetetramine: CP–MAS 13C ‐ NMR. *Journal of Applied Polymer Science* 56(12): 1645-1650

Pizzi A, Valenezuela J, Westermeyer C (1994) Low formaldehyde emission, fast pressing, pine and pecan tannin adhesives for exterior particleboard. *HolzalsRoh-und Werkstoff* 52(5): 311-315

Ragan MA, Glombitza KW (1986) Phlorotannins, brown algal polyphenols. *Progress in Phycological Research* 4: 177-241

Ramesh VC, Dodwell DP (1981) Wood treatment process and product thereof. US Patent 4276329

Ray SS, Okamoto M (2003) Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in polymer Science* 28(11): 1539-1641

Rebitzer G, Ekvall T, Frischknecht R, Hunkeler D, Norris G, Rydberg T, Schmidt WP, Suh S, Weidemai BP, Pennington DW (2004) Life cycle assessment: Part 1: Framework, goal and scope definition, inventory analysis, and applications. *Environment International* 30(5): 701-720

Richter K (1995) Life cycle analysis of wood products. In proceedings workshop: Life-cycle analysis - a challenge for forestry and forest industry, the European Forest Institute and the Federal Research Centre for Forestry and Forest Products, Hamburg, Germany 69-77

Robinson PL, Blasser JE, Lake MA, McIntyre CR (2005) Leaching Tests of ‘Controlled’ Borate Systems. Proceedings American Wood Preservers’ Association 101: 75-83

Roux DG, Ferreira D, Hundt HKL, Malan E (1975) Structure, stereochemistry, and reactivity of natural condensed tannins as a basis for their extended industrial application. *Applied Polymer Symposium* 28(1): 335-353

Rowe JW, Conner AH (1979) *Extractives in eastern hardwoods - A review* (No. FSGTR-FPL-18). Forest Products Laboratory. Forest Service U.S. Department of Agriculture. Madison, Wisconsin

Russell LJ, Marney DCO, Humphrey DG, Hunt AC, Dowling VP, Cookson LJ (2007) Combining fire retardant and preservative systems for timber products in exposed applications - state of the art review. *Forest and Wood Products Research and Development Corporation*, Australia

Rusu E, Rusu G, Dorohoi DO (2009) Influence of temperature on structures of polymers with ε-caprolactam units studied by FT-IR spectroscopy. *Polimery* 54(5): 347-353

Sauget A, Zhou X, Pizzi A (2014) Tannin-resorcinol-formaldehyde resin and flax fiber biocomposites. *Journal of Renewable Materials* 2(3): 173-181

SAWPA (2014) South African Wood Preservers Association. Understanding timber preservation. Available from http://www.sawpa.org.za/understanding.html

Scalbert A, Cahill D, Dirol D, Navarrete MA, De Troya MT, Van Leemput M (1998) A tannin/copper preservation treatment for wood. *Holzforschung* 52(2): 133-138

Schneider MH (1994) Wood Polymer Composites. *Wood and Fiber Science* 26(1): 142-151

Schneider MH, Brebner KI, Hartley ID (1991) Swelling of a cell lumen filled and a cell-wall bulked wood polymer composite in water. *Wood and Fiber Science* 23(2): 165-172

Schoeman MW, Lloyd JD, Manning MJ (1998) Movement of borates in a range of timber species at various moisture contents. The International Research Group on Wood Preservation, IRG/WP/98-30181. IRG Secretariat, Stockholm, Sweden

Schubert DM (2003) Borates in industrial use. In *Group 13 Chemistry III: Industrial applications*, 105 Structure and bonding. Mingos DMP (Managing Ed.), Roesky HW, Atwood DA (Volume Ed.), Springer Berlin Heidelberg. 105:1-40

Schubert DM, Manning MJ (1997) Compositions and methods for preserving wood products. US Patent 5612094

Schultz TP, Nicholas DD, Preston AF (2007) A brief review of the past, present and future of wood preservation. *Pest Management Science* 63(8): 784-788

Schwarze FWMR, Baum S (2000) Mechanisms of reaction zone penetration by decay fungi in wood of beech (*Fagus sylvatica*). *New Phytologist* 146: 129-140

Scorei R (2012) Is boron a prebiotic element? A mini-review of the essentiality of boron for the appearance of life on Earth. *Origins of Life and Evolution of Biospheres* 42(1): 3-17

Sevim F, Demir F, Bilen M, Okur H (2006) Kinetic analysis of thermal decomposition of boric acid from thermogravimetric data. *Korean Journal of Chemical Engineering* 23(5): 736-740

Shabala S, Munns R (2012) Salinity stress: physiological constraints and adaptive mechanisms. In *Plant Stress Physiology*. Shabala S (Ed.), 59-93

Shah AP, Gupta RK, Gangarao HV, Powell CE (2002) Moisture diffusion through vinyl ester nanocomposites made with montmorillonite clay. *Polymer Engineering and Science* 42(9): 1852-1863

Shiozawa K (1991) Wood preservative composition and process for treating wood with the same. US Patent 5207823

Shrimpton DM, Whitney HS (1968) Inhibition of growth of blue stain fungi by wood extractives. *Canadian Journal of Botany* 46(6): 757-761

Simon JM, Smith RA (2000) Borate raw materials. *Glass Technology-European Journal of Glass Science and Technology Part A* 41(6): 169-173

Simsek H, Baysal E, Peker H (2010) Some mechanical properties and decay resistance of wood impregnated with environmentally-friendly borates. *Construction and Building Materials* 24(11): 2279-2284

Singh T, Singh AP (2012) A review on natural products as wood protectant. *Wood Science and Technology* 46(5): 851-870

Sjostrom E (1993) Wood chemistry: fundamentals and applications. Second edition ed. San Diego: Academic press. 292

Slimak KM, Slimak RA (1998) Enhancing the strength, moisture resistance, and fire-resistance of wood, timber, lumber, similar plantderived construction and building materials, and other cellulosic materials. US Patent 6146766

Smith RA (1985) Boric oxide, boric acid, and borates. In Ullmann's Encyclopedia of Industrial Chemistry. Gerhartz W (Ed.), 5th edition, vol A4. VCH, Weinheim, pp. 263-280

Smith, D.N., Williams, A.I. (1969) Wood preservation by boron diffusion process- effect of moisture content on diffusion time. Journal Institute of Wood Science 22: 3-10.

Sogutlu C, Demirci Z, Dongel N, Imirzi HO, Doruk S, Yalınkılıc AC, Design B (2011) The determination of the resistance to burning of some wood types impregnated with sodium borate solution. *Wood Research* 56(2): 233-244

Son DW, Kang MR, Kim JI, Park SB (2012) Fire performance of the wood treated with inorganic fire retardants. *Journal of the Korean Wood Science and Technology* 40(5): 335-42

Spiller D (1948) Toxicity of boric acid to the common house borer (*Anobium punctatum* de Geer). *New Zealand Journal Science and Technology* Sect. B, 30(3):129-139

Srivastava VK, Pizzi A (2014) Characterization and preparation of wood-furanic foams. *Journal of Renewable Materials* 2(3): 201-206

Svanæs J (2010) Environmental friendly timber bridges–Environmental improvement through product development. Proceedings of the International Conference Timber Bridges Lillehammer, Norway, 119-122

Tamblym N, Da Costa EWB, Gay FJ (1959) Preservative treatments for plywood by momentary dipping of green veneer. Commonwealth Scientific and Industrial Research Organization (Melbourne, Australia), *Division of Forest Products Technological Paper* No. 6: 8

Tamblyn N, Gordon A (1950) Control of borer attack in plywood by use of preservatives in the glue. *Forest Products News Letter* 180: 1-2

Tanimura S, Kadomoto R, Tanaka T, Zhang YJ, Kouno I, Kohno M (2005) Suppression of tumor cell invasiveness by hydrolyzable tannins (plant polyphenols) via the inhibition of matrix metalloproteinase-2/-9 activity. *Biochemical and Biophysical Research Communications* 330(4): 1306-1313

Tascioglu C, Yalcin M, de Troya T, Sivrikaya H (2012) Termiticidal properties of some wood and bark extracts used as wood preservatives. *BioResources* 7(3): 2960-2969

Taylor AM, Gartner BL, Morrell JJ, Tsunoda K (2006) Effects of heartwood extractive fractions of Thuja plicata and Chamaecyparis nootkatensis on wood degradation by termites or fungi. *Journal of Wood Science* 52(2): 147-153

Temiz A, Alfredsen G, Eikenes M, Terzıev N (2008) Decay resistance of wood treated with boric acid and tall oil derivates. *Bioresource Technology* 99(7): 2102-2106

Temiz A, Gezer ED, Yildiz UC, Yildiz S (2008) Combustion properties of alder (*Alnus glutinosa L.*) *Gaertn. subsp. barbata* (CA Mey) Yalt.) and southern pine (*Pinus sylvestris L.*) wood treated with boron compounds. *Construction and Building Materials* 22(11): 2165-2169

Temiz A, Kartal SN, Alfredsen G, Eikenes M, Demirtas I (2006) Fungal and termite resistance of wood treated with 4-methoxytrityl tetrafluoroborate. *Holz als Roh-und Werkstoff* 64(5): 411-414

Theng BKG (1974) The chemistry of clay-organic reactions. The Chemistry of Clay-Organic Reactions. Wiley, New York 221-238

Thevenon MF, Pizzi A, Haluk JP (1997) Non-toxic albumin and soja protein borates as ground-contact wood preservatives. *European Journal of Wood and Wood Products* 55(5): 293-296

Thevenon MF, Pizzi A, Haluk JP (1998a) Condensed tannins and boric acid for environment friendly wood preservatives. In Proceedings 2nd International Electronic Conference on Synthetic Organic Chemistry (ECSOC-2). Poster presentation, Available from http://www.mdpi.org/ecsoc/

Thévenon MF, Pizzi A, Haluk JP (1998b) Albumin borate: a new non-toxic, wide spectrum, long term wood preservative. The International Research Group on Wood Preservation, IRG/WP 98-30167. IRG Secretariat, Stockholm, Sweden

Thévenon MF, Pizzi A, Haluk JP (1998c) One-step tannin fixation of non-toxic protein borates wood preservatives. *Holz als Roh und Werkstoff* 56: 90

Thévenon MF, Pizzi A, Haluk JP (1999) Potentialities of protein borates as low toxic, long term wood preservatives – preliminary trials. The International Research Group on Wood Preservation, IRG/WP 99-30212. IRG Secretariat, Stockholm, Sweden

Thévenon MF, Pizzi A, Haluk JP, Zaremski A (1998d) Normalized biological tests of protein borates wood preservatives. *Holz als Roh und Werkstoff* 56: 162

Thévenon MF, Tondi G, Leménager N, Wieland S, Pizzi A(2011) Tannin resin-boron for outdoor wood protection and fire retardancy. The International Research Group on Wood Preservation, IRG/WP 11-30567. IRG Secretariat, Stockholm, Sweden

Thevenon MF, Tondi G, Pizzi A (2009) High performance tannin resin-boron wood preservatives for outdoor end-uses. *European Journal of Wood and Wood Products* 67(1): 89-93

Thévenon MF, Tondi G, Pizzi A (2010) Friendly wood preservative system based on polymerized tannin resin-boric acid for outdoor applications. *Maderas. Ciencia y tecnolog á* 12(3): 253-257

Thevenon MF, Tondi G, Pizzi A (2011) Environmentally friendly wood preservative system based on polymerized tannin resin-boric acid for outdoor applications. *Maderas. Ciencia y tecnologia* 12(3): 253-257

Tikhomirova AV, Peresypkina EV, Virovets AV, Cherkasova TG (2013) Synthesis and crystal structure of lanthanum (III) Iodomercurate (II) complexes with ε-Caprolactam. *Russian Journal of Inorganic Chemistry* 58(5): 534-542

Tillman DA (2012) Wood combustion: principle, processes, and economics. Burlington: Elsevier Science

Timell TE (1986) Compression wood in gymnosperms, Volume 1. Berlin: Springer, pp.706

Tomak ED, Viitanen H, Yildiz UC, Hughes M (2011) The combined effects of boron and oil heat treatment on the properties of beech and Scots pine wood. Part 2: Water absorption, compression strength, color changes, and decay resistance. *Journal of Materials Science* 46(3): 608-615

Tondi G, Haurie L, Wieland S, Petutschnigg A, Lacasta A, Monton J (2014) Comparison of disodium octaborate tetrahydrate - based and tannin - boron - based formulations as fire retardant for wood structures. *Fire and Materials* 38(3): 381-390

Tondi G, Palanti S, Wieland S, Thevenon MF, Petutschnigg A, Schnabel T (2012a) Durability of tannin-boron-treated timber. *BioResources* 7(4): 5138-5151

Tondi G, Petutschnigg A (2014) Middle infrared (ATR FT-MIR) characterization of industrial tannin extracts. Industrial Crops and Products, http://dx.doi.org/10.1016/j.indcrop.2014.11.005

Tondi G, Schnabel T, Wieland S, Petutschnigg A (2013a) Surface properties of tannin treated wood during natural and artificial weathering. *International Wood Products Journal* 4(3): 150-157

Tondi G, Thevenon, MF, Mies B, Standfest G, Petutschnigg A, Wieland S (2013b) Impregnation of scots pine and beech with tannin solutions: effect of viscosity and wood anatomy in wood infiltration. *Wood Science and Technology* 47(3): 615-626

Tondi G, Wieland S, Lemenager N, Petutschnigg A, Pizzi A, Thevenon MF (2012b) Efficacy of tannin in fixing boron in wood: fungal and termites resistance. *Bioresources* 7(1): 1238-1252

Tondi G, Wieland S, Wimmer T, Thevenon MF, Pizzi A, Petutschnigg A(2012a) Tannin-boron preservatives for wood buildings: Mechanical and fire properties. *European Journal of Wood and Wood Products* 70 (5): 689-696

Tondi G, Hu JB, Thevenon MF (2015) Advanced tannin-based wood preservatives. *Forest Products Journal* 65(3/4): In press

Toussaint-Davergne E, Souloungang a P, Gerardin P, Loubinoux B (2000) Glycerol/Glyoxal: A new boron fixation system for wood preservation and dimensional stabilization. *Holzforschung* 54(2):123-126

Tsunashima A, Brindley GW, Bastovanov M (1981) Adsorption of uranium from solutions by montmorillonite; compositions and properties of uranyl montmorillonites. *Clays and Clay Minerals, 29*(1): 10-16

Türker OC, Böcük H, Yakar A (2013) The phytoremediation ability of a polyculture constructed wetland to treat boron from mine effluent. *Journal of Hazardous Materials* 252-253: 132-141

Updegraff DM (1969) Semimicro determination of cellulose in biological materials. *Analytical Biochemistry* **32** (3): 420–424

Vaia RA, Giannelis EP (1997) Polymer melt intercalation in organically-modified layered silicates: model predictions and experiment. *Macromolecules* 30(25): 8000-8009

Vaia RA, Jandt KD, Kramer EJ, Giannelis EP (1995) Kinetics of Polymer Melt Intercalation. *Macromolecules* 28(24): 8080-8085

Varma A, Kolli BK, Paul J, Saxena S, König H (1994) Lignocellulose degradation by microorganisms from termite hills and termite guts: A survey on the present state of art. *FEMS microbiology reviews* 15(1): 9-28

Van Rijswijk K, Teuwen JJE, Bersee HEN, Beukers A (2009) Textile fiber-reinforced anionic polyamide-6 composites. Part I: The vacuum infusion process. *Composites Part A: Applied Science and Manufacturing*, 40(1):1-10

Vázquez G, Fontenla E, Santos J, Freire MS, González-Álvarez J, Antorrena G (2008) Antioxidant activity and phenolic content of chestnut (*Castanea sativa*) shell and eucalyptus (Eucalyptus globulus) bark extracts. *Industrial Crops and Products* 28(3): 279-285

Vek V, Oven P, Humar M (2013) Phenolic extractives of wound-associated wood of beech and their fungicidal effect. *International Biodeterioration and Biodegradation* 77: 91-97

Venkataraman NV, Vasudevan S (2000) Conformation of an alkane chain in confined geometry: cetyl trimethyl ammonium ion intercalated in layered CdPS3. *The Journal of Physical Chemistry B* 104(47): 11179-11185

Vieira MC, Lelis RCC, da Silva BC, de Lima Oliveira G (2011) Tannin extraction from the bark of *Pinus oocarpa* var. *oocarpa* with sodium carbonate and sodium bisulfite. *Floresta e Ambiente*, 18(1): 1-8

Vinden P, Burton RJ, Vaioleti TM (1991) Gaseous or vapor phase treatment of wood with boron preservatives. U.S. Patent No. 5,024,861. Washington, DC: U.S. Patent and Trademark Office.

Walker LE (1997) Quaternary ammonium carboxylate and borate compositions and preparation thereof. US Patent 5641726

Walker LE (1999a) Quaternary ammonium carboxylate and borate compositions and preparation thereof. US Patent 5891921

Walker LE (1999b) Waterproofing and preservative compositions and preparation thereof. US Patent 5855817

Walker LE (2000) Quaternary ammonium carboxylate and borate compositions and preparation thereof. US 6087303

Walker LE, Tseng C, Kempinska Jr, Charles C (2003) Boron compound/amine oxide compositions. US Patent 6508869

Wang L, Wang A (2008) Adsorption properties of Congo Red from aqueous solution onto surfactant-modified montmorillonite. *Journal of Hazardous Materials* 160(1) : 173-180

Wang Z, Pinnavaia TJ (1998) Nanolayer reinforcement of elastomeric polyurethane. *Chemistry of Materials* 10(12): 3769-3771

Wesite of OAK WILT http://www.oakwilt.com/articles13001/anatomy2.html

Werner F, Richter K (2007) Wooden building products in comparative LCA. *The International Journal of Life Cycle Assessment* 12(7): 470-479

West H (1988) Kinetics and mechanism of wood-isocyanate reactions. Ph.D. thesis. University of North Wales, Bangor, UK

WHO/FAO/IAEA (1996) Trace elements in human nutrition and health. World Health Organization, Geneva. 175-179

Widom M, Mihalkovič M (2008) Symmetry-broken crystal structure of elemental boron at low temperature. *Physical Review B* 77(6): 64-113

Williams LH (1997) Laboratory and field testing of borates used as pesticides. Second International Conference on wood protection with diffusible preservatives and pesticides. Forest Product Society, Madison, Wisconsin, pp. 14-19

Williams RS (2005) Weathering of Wood. Handbook of wood chemistry and wood composites, pp.140

Wisniak J (2005) Borax, boric acid, and boron-from exotic to commodity. *Indian Journal of Chemical Technology* 12(4): 488-500

Woodrow RJ, Grace JK, Yates JR (1999) Hawaii's Termites-an Identification Guide. Cooperative Extension Service, College of Tropical Agriculture and Human Resources, University of Hawaii at Manoa, 1-6

Woods WG (1994) An introduction to boron: history, sources, uses, and chemistry. *Environmental Health Perspectives* 102(Suppl 7): 5-11

Wypych G (2003) Handbook of material weathering. 5th Edition, ChemTec Publishing

XP X 41-542 (1995) Produits de préservation du bois - Produit de traitement anti-termites des sols, murs, fondations et maçonneries - Épreuve de vieillissement accéléré des matériaux traités avant essais biologiques - Épreuve de percolation.

Xue FL, Zhao GJ (2008) Optimum preparation technology for Chinese fir wood/Ca-montmorillonite (Ca-MMT) composite board. *Forestry Studies in China* 10(3): 199-204

Yalinkilic MK, Dwianto W, Imamura Y, Takamashi M (1998a) A new process for in situ polymerization of vinyl monomers in wood to delay boron leaching. The International Research Group on Wood Preservation, IRG/WP/98. IRG Secretariat, Stockholm, Sweden

Yalinkilic MK, Dwianto W, Imamura Y, Tsunoda K, Takamashi M (1999a) Biological resistance of steam –compressed wood pretreated with boric compounds. The International Research Group on Wood Preservation, IRG/WP 99-30190. IRG Secretariat, Stockholm, Sweden

Yalinkilic MK, Gezer ED, Takahashi M, Demirci R, Imamura Y (1999b) Boron addition to non- or low-formaldehyde cross-linking reagents to enhance biological resistance and dimensional stability of wood. *Holz als Roh und Werkstoff* 57(5): 351-357

Yalinkilic MK, Imamura Y, Takahashi M, Yalinkilic AC (1999c) In situ polymerization of vinyl monomers during compressive deformation of wood treated with boric acid to delay boron leaching. *Forest Products Journal* 49(2): 43-51

Yalinkilic MK, Yoshimura T, Takahashi M (1998b) Enhancement of the biological resistance of wood by phenylboronic acid treatment. *Wood Science and Technology* 44(2): 152-157

Yalinkilic MK, Yusuf S, Yoshimura T, Su W, Tsunoda K, Takamashi M (1997) Incorporation of phenyl boronic acid treatment with vapour phase formalization. The International Research Group on Wood Preservation, IRG/WP 97-40083. IRG Secretariat, Stockholm, Sweden

Yamaguchi H (2003) Silicic acid: boric acid complexes as wood preservatives. Ability of treated wood to resist termites and combustion. *Wood Science Technology* 37(3-4): 287-297

Yamaguchi H (2005) Silicic acid/boric acid complexes as ecologically friendly wood preservatives. *Forest Products Journal* 55(1): 88-92

Yamaguchi H, Okuda KI (1998) Chemically modified tannin and tannin-copper complexes as wood preservatives. *Holzforschung* 52(6): 596-602

Yang LL, Lee CY, Yen KY (2000) Induction of apoptosis by hydrolyzable tannins from Eugeniajambos L. on human leukemia cells. *Cancer Letters* 157(1): 65-75

Yoon KB, Sung HD, Hwang YY, Noh SK, Lee DH (2007) Modification of montmorillonite with oligomeric amine derivatives for polymer nanocomposite preparation. *Applied Clay Science* 38(1): 1-8

Yu X, Sun D, Li X (2011) Preparation and characterization of urea-formaldehyde resin-sodium montmorillonite intercalation-modified poplar. *Journal of Wood Science* 57(6): 501-506

Zabalza Bribián I, Valero Capilla A, Aranda Usón A (2011) Life cycle assessment of building materials: Comparative analysis of energy and environmental impacts and evaluation of the eco-efficiency improvement potential. Building and Environment, 46(5): 1

Zanetti M, Lomakin S, Camino G (2000) Polymer layered silicate nanocomposites. *Macromolecular Materials and Engineering* 279(1): 1-9

Zerda AS, Lesser AJ (2001) Intercalated clay nanocomposites: morphology, mechanics, and fracture behavior. *Journal of Polymer Science Part B: Polymer Physics* 39(11): 1137-1146

Zhao Y, Wang K, Zhu F, Xue P, Jia M (2006) Properties of poly (vinyl chloride)/wood flour/montmorillonite composites: effects of coupling agents and layered silicate. *Polymer Degradation and Stability* 91(12): 2874-2883

Zhao Z, Tang T, Qin Y, Huang B (2003) Relationship between the continually expanded interlayer distance of layered silicates and excess intercalation of cationic surfactants. *Langmuir* 19(22): 9260-9265

Zhu J, He H, Zhu L, Wen X, Deng F (2005) Characterization of organic phases in the interlayer of montmorillonite using FTIR and ^{13}C NMR. *Journal of Colloid and Interface Science* 286(1): 239-244

Zimmermann T, Pöhler E, Geiger T (2004) Cellulose fibrils for polymer reinforcement. *Advanced Engineering Materials* 6(9): 754-761

Annex A. Strategies proposed for reducing boron leaching (Obanda et al. 2008)

Item	Strategy/system	Proponents
1	Surface treatments	Peylo and Willeitner (1995a,b), Homan and Militz (1995), Mohareb et al. (2002), Hedley and Page (2006)
2	Envelope treatment (over-treatment)	Amburgey et al. (2003), Gauntt and Amburgey (2005)
3	Wood bulking resins and water repellants	Ramesh and Dodwell (1981), Yalinkilic et al. (1997), Cui and Kamdem (1999), Yalinkilic et al. (1999b), Mohareb et al. (2002), Hutter et al. (2004)
4	Organo boron compounds (boronic and boric acids)	Liu et al. (1994), Yalinkilic et al. (1998a)
5	Precipitation of organo soluble salts within wood	Lin et al. (2001)
6	Combination of biocides and non-biocidal chemicals	Kartal and Green (2003), Kartal and Imamura (2003), Akbulut et al. (2004)
7	Metallo-borates	Schubert and Manning (1997), Lloyd et al. (2001), Furuno et al. (2003, 2006), Freeman and Amburgey (1997), Amburgey and Freeman (2000)
8	Ammoniacal and amine metallo-borates	Farber (1951), Malouf and Docks (1991), Shiozawa (1991), Barth and Hartner (1994), Walker (1997, 1999a,b, 2000), Walker et al. (2003), Lloyd and Fogel (2005)
9	Stabilized boroesters	Maynard (1993), Hedley et al. (2000), Humphrey et al. (2002), Carr et al. (2005)
10	Protein borates	Thevenon et al. (1998a,b, 1999), Thevenon and Pizzi (2003), Ratajczak and Mazela (2007)
11	Tannin auto condensation	Thevenon et al. (1998c,d, 1999), Pizzi and Baecker (1996)
12	In situ polymerization	Ozaki et al. (2001), Baysal et al. (2004), Cui and Kamdem (1999), Yalinkilic et al. (1998b), Yalinkilic et al. (1999b)
13	Vaporization of organic boron compounds and boric acid	Baysal and Yalinkilic (2005)

(Continued)

Annex A *(concluded)*

Item	Strategy/system	Proponents
14	Boron-silicates	Du-Fresne and Campbell (1967), Kazunobu (1995), Slimak and Slimak (1998), Yamaguchi (2003), Yamaguchi (2005)
15	Physical modification of wood (compressive deformation)	Yalinkilic et al. (1999a), Baysal and Yalinkilic (2005)

Annex B. Comparative result of LCA for wood component treated with preservative of penta, ACQ and borate (Bolin and Smith 2011a, b, c)

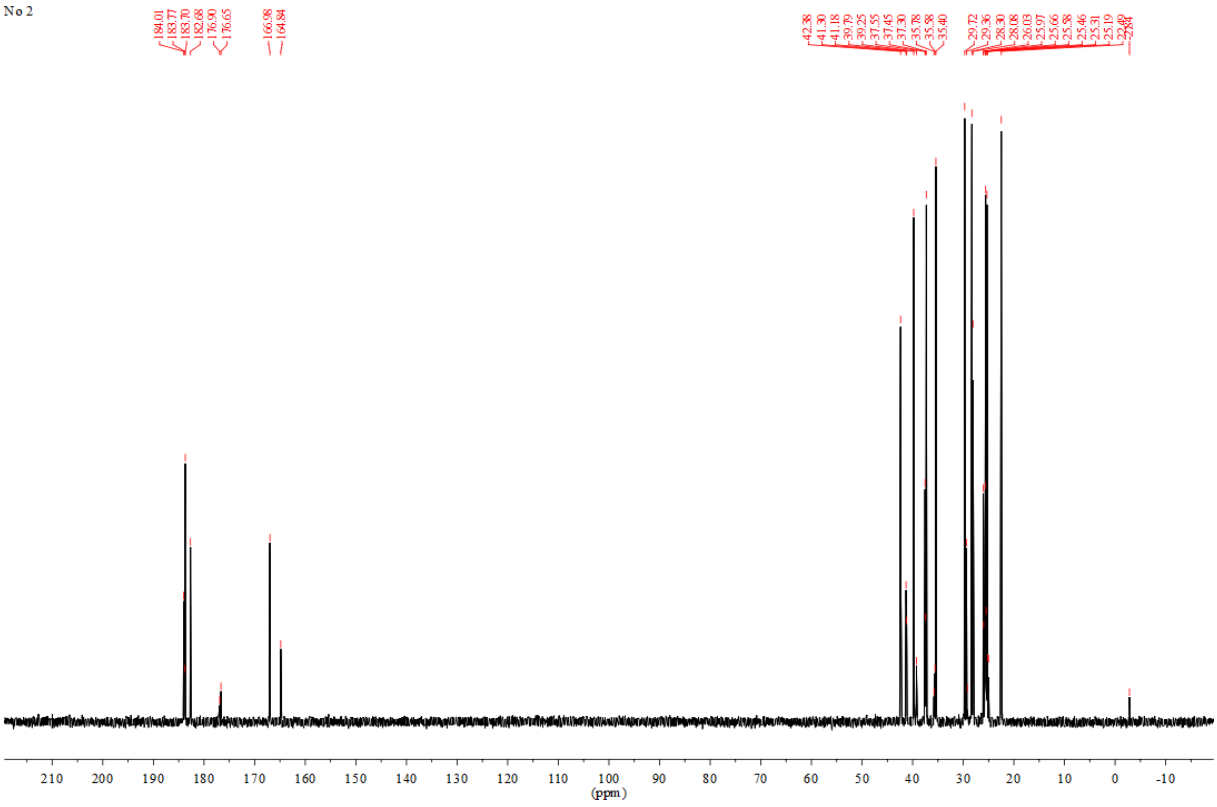
Component and Material / Impact indicators		Utility pole			Deck		Framing	
		Penta	Concrete	Steel	ACQ	WPC	Borate	Steel
Fossil fuel use		1	4	2	1	14	1	4
Water use		1	4	2	1	3	1	83
Environmental impacts	Greenhouse gas	1	20	10	1	3	1	1.8
	Acidification	1	77	54	1	4	1	3.5
	Eutrophication	1	5	1.5	1	1	1	3.3
	Ecological toxicity	1	14	4	1	2	1	2.5
	Smog emissions	1	1/2	1/5	1	2	1	2.8
Total energy use value (fossil fuel, biogenic, and renewable resources)		1	3	1.7	1	8.5	1	3.6
Ratio of fossil fuel source		75%	94%	89%	50%	100%	100%	100%

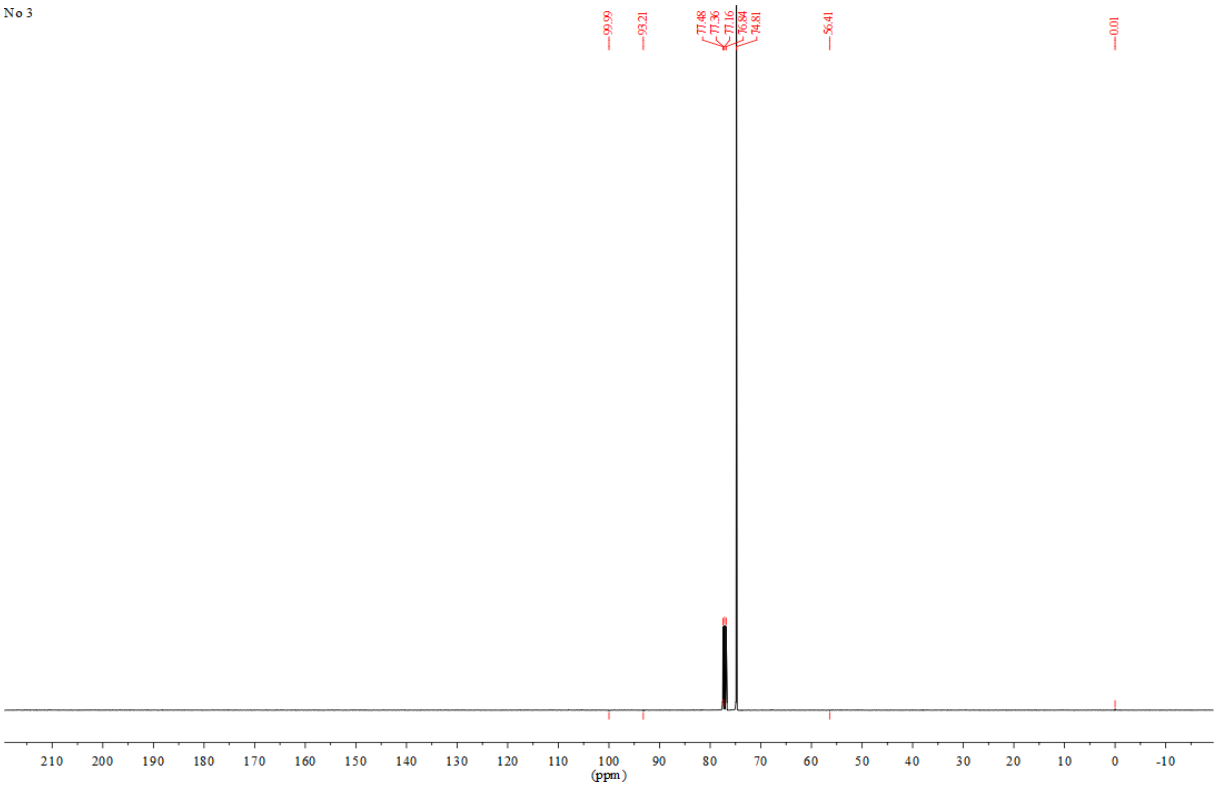
Note: Impact indicator of each treated wood component is “1”, and others refer to “impact indicator of wood component”.

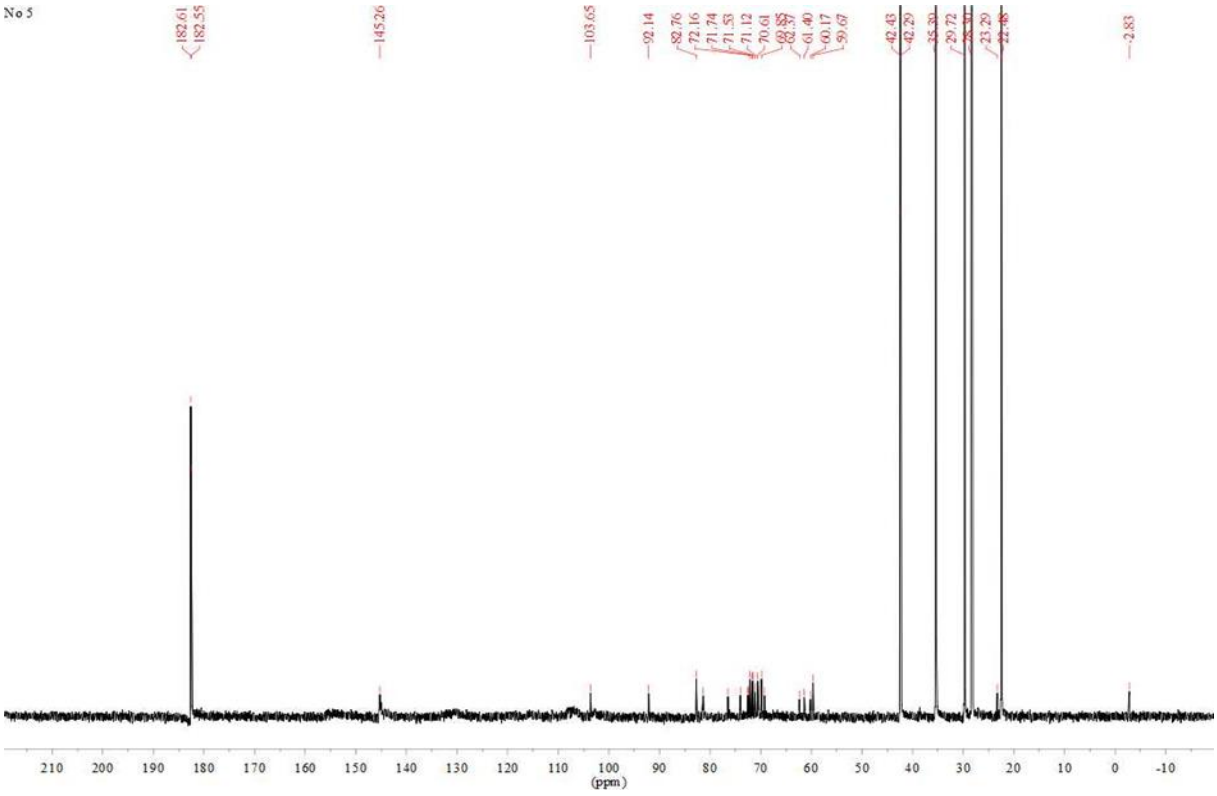
Annex C. Visual rating criteria to express the attack level of the wood samples and efficiency evaluation of the treatment (EN117, EN118)

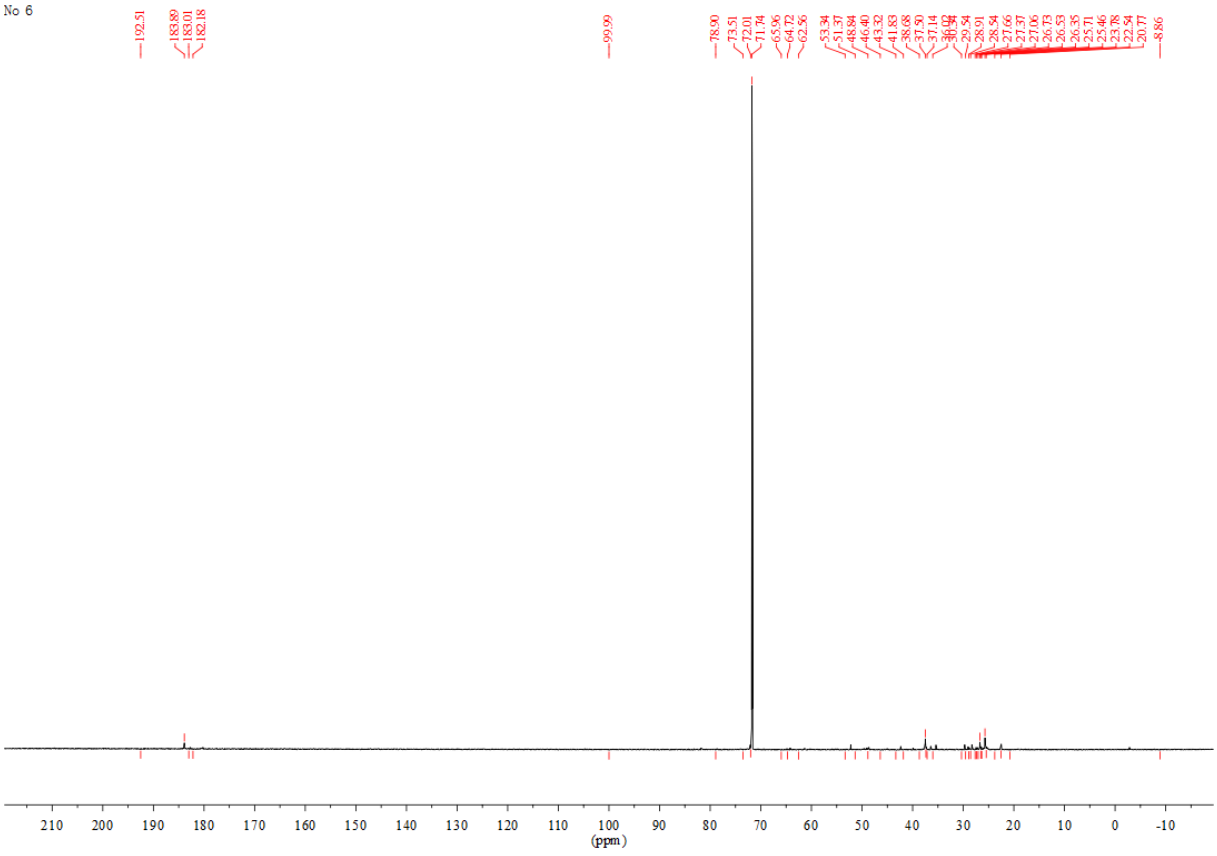
Levels of attack	Description
0	no attack
1	attempted attack: i) superficial erosion of insufficient depth to be measured on an unlimited area of the test specimen; or ii) attack to depth of 0.5 mm provided that this is restricted to an area or areas not more than 30mm^2 in total; or iii) combination i) and ii)
2	slight attack: i) erosion of 1 mm in depth limited to not more than 1/10 of the surface area of the test specimen; or ii) single tunnelling to a depth of up to 3 mm; or iii) combination i) and ii)
3	average attack: i) erosion of < 1 mm in depth over more than 1/10 of the surface area of the test specimen; or ii) erosion of > 1mm to < 3 mm in depth limited to not more than 1/10 of the surface area of the test specimen; or iii) isolated tunnelling of a depth of > 3 mm not enlarging to form cavities; or iv) any combination of i), ii) or iii)
4	strong attack: i) erosion of > 1mm to < 3 mm in depth of more than 1/10 of the surface area of the test specimen; or ii) tunnelling penetrating to a depth of > 3 mm and enlarging to form a cavity in the body of the test specimen; or iii) combination of i) and ii)
Criteria to pass the termite test	The treatment should protect the wood, i.e. none of the tests specimens show a degree of attack greater than level 2 with only one test specimen showing a degree of attack of level 2.

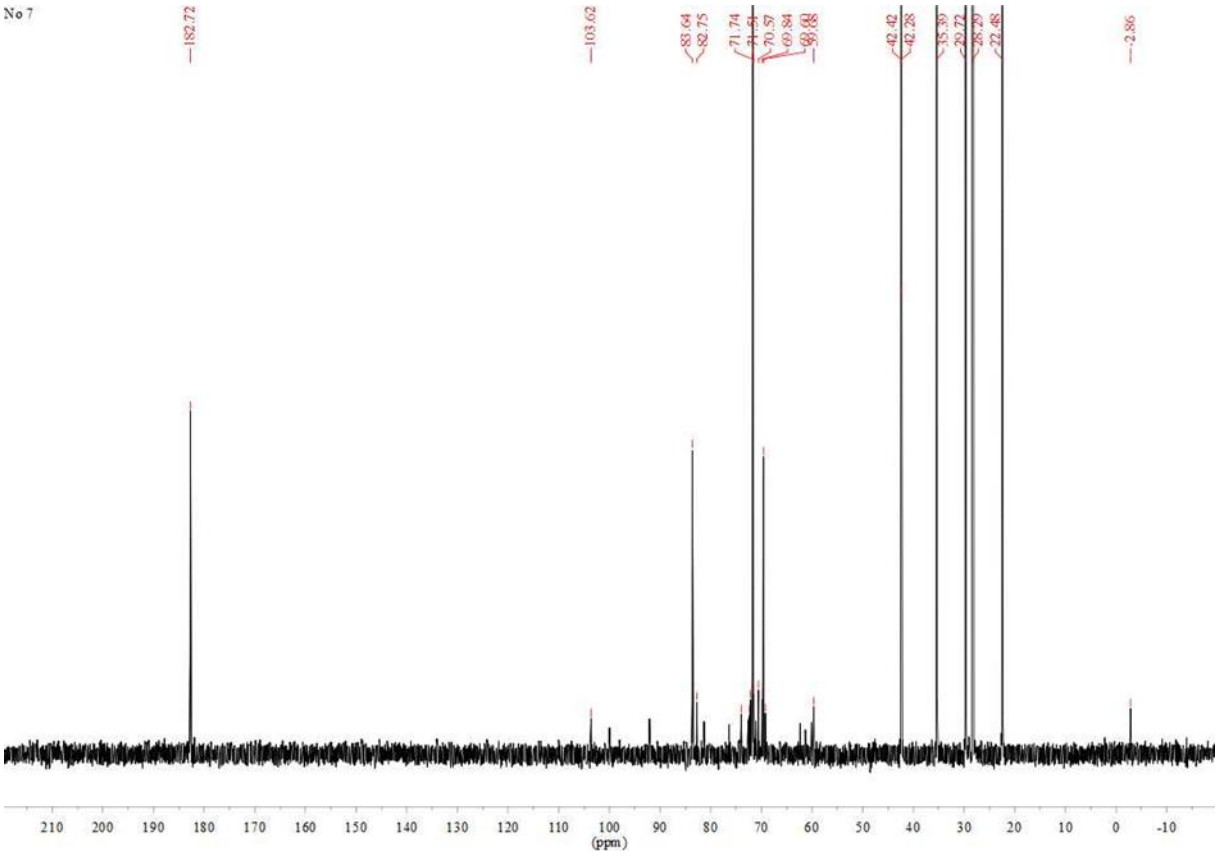
Annex D. Liquid ^{13}C-NMR spectra of tannin-boron-caprolactam series

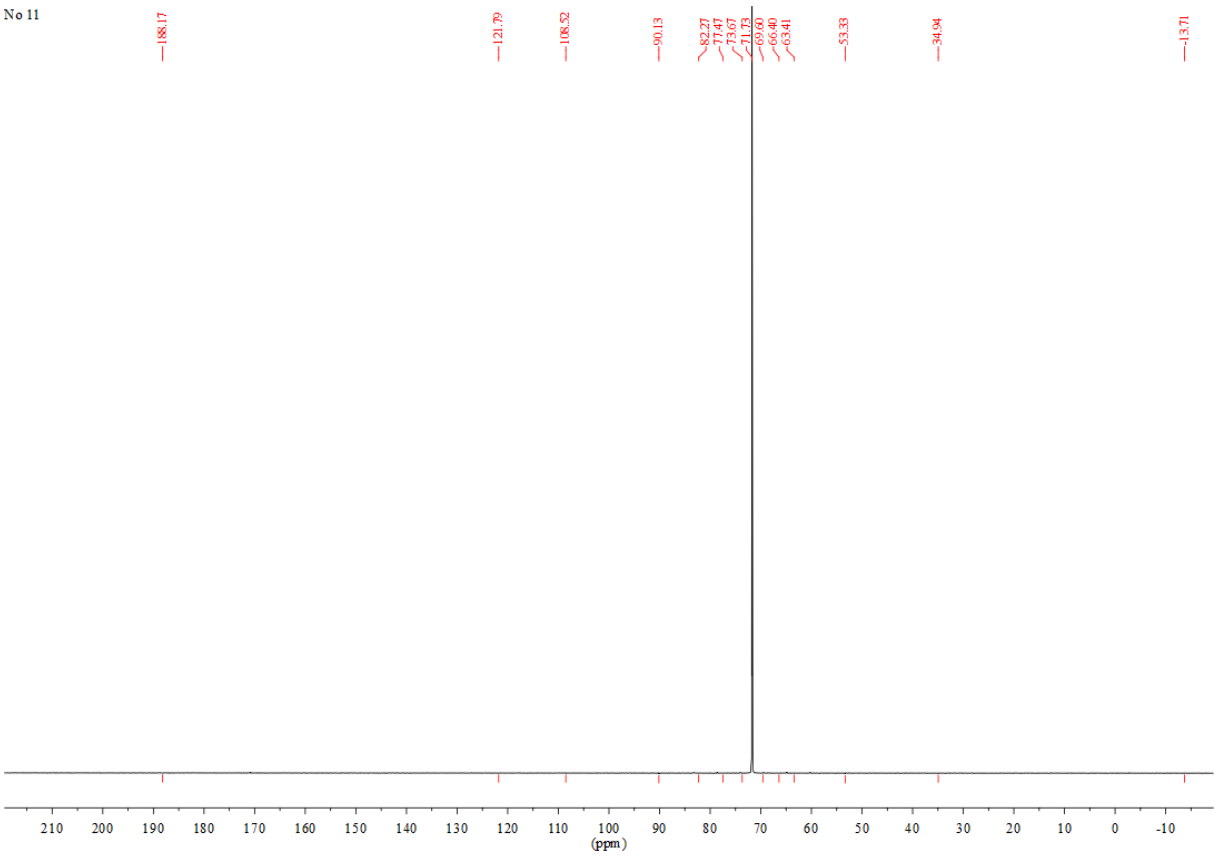


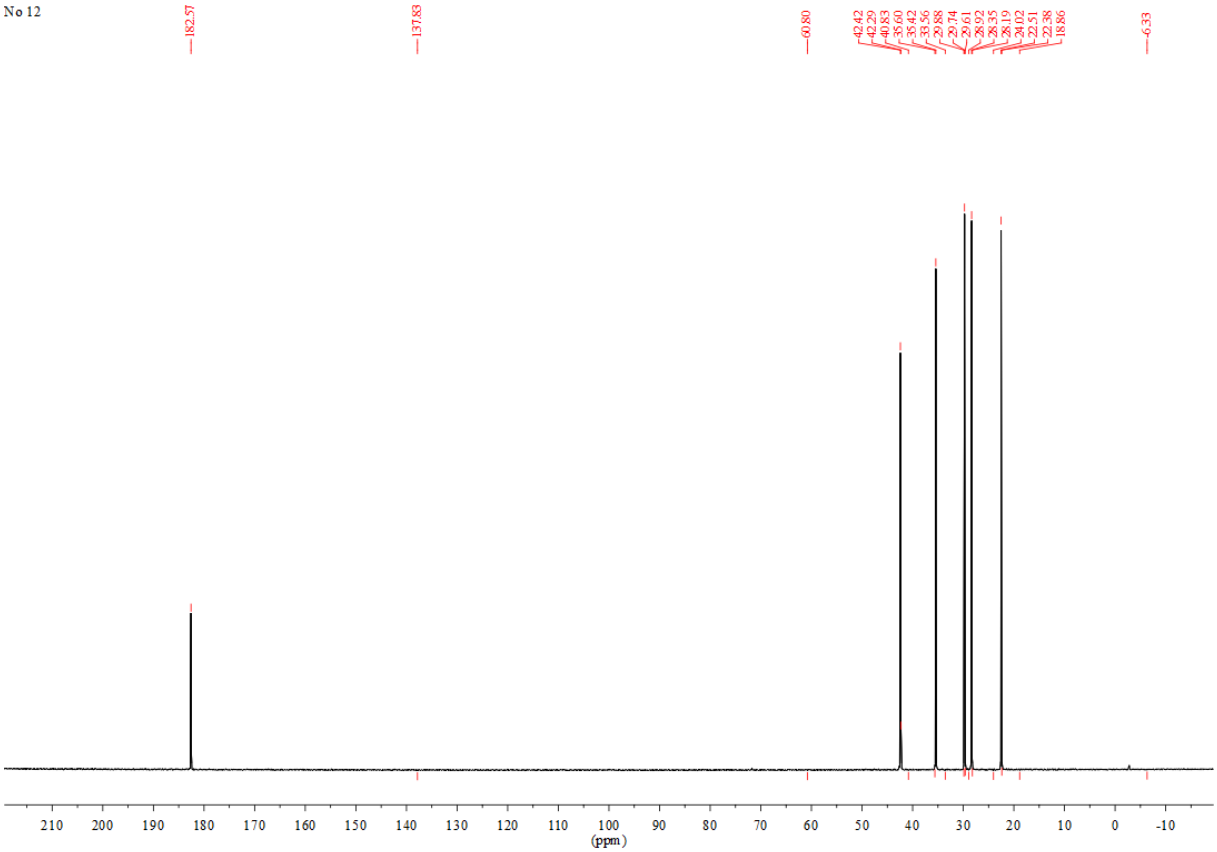


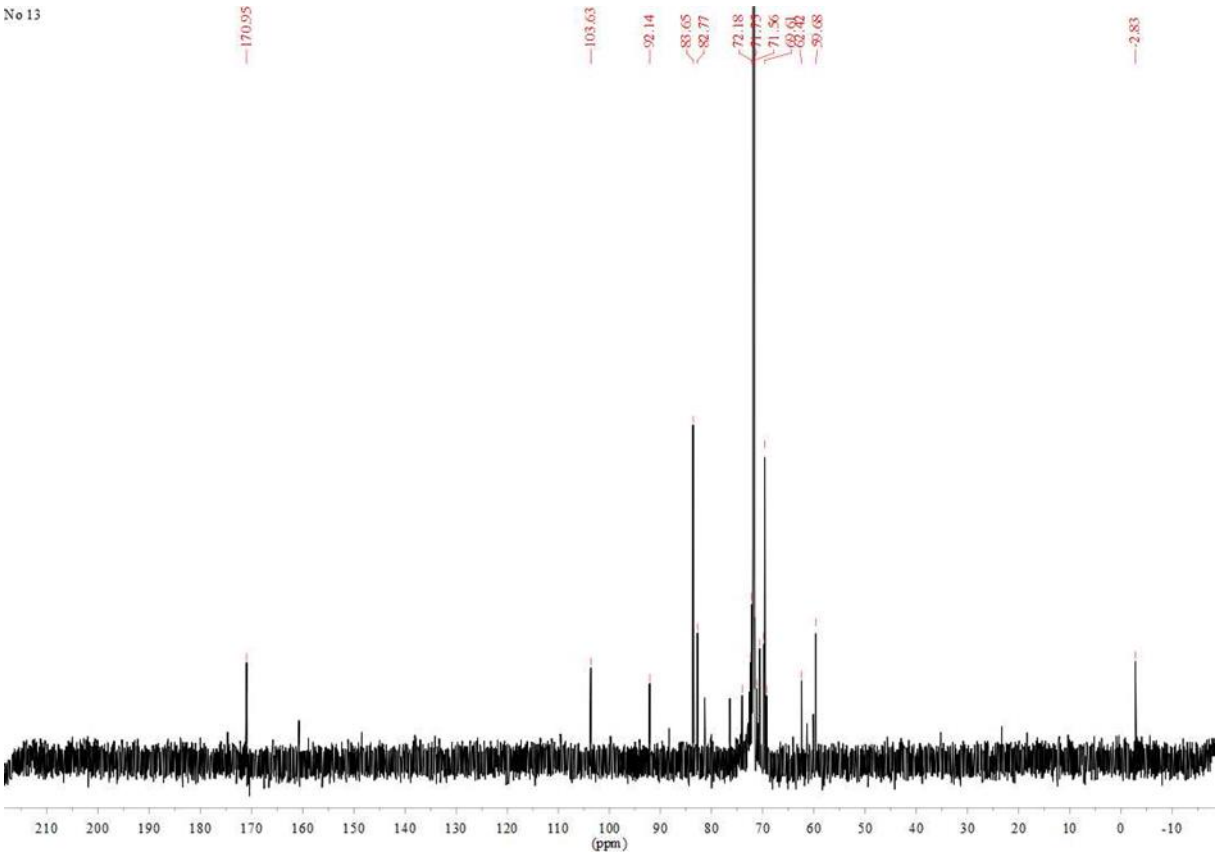

No 5
182.61
182.55
145.26
103.65
92.14
82.76
72.16
71.74
71.53
71.12
70.61
61.40
60.17
59.67
42.43
42.29
35.30
29.72
23.29
22.48
2.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

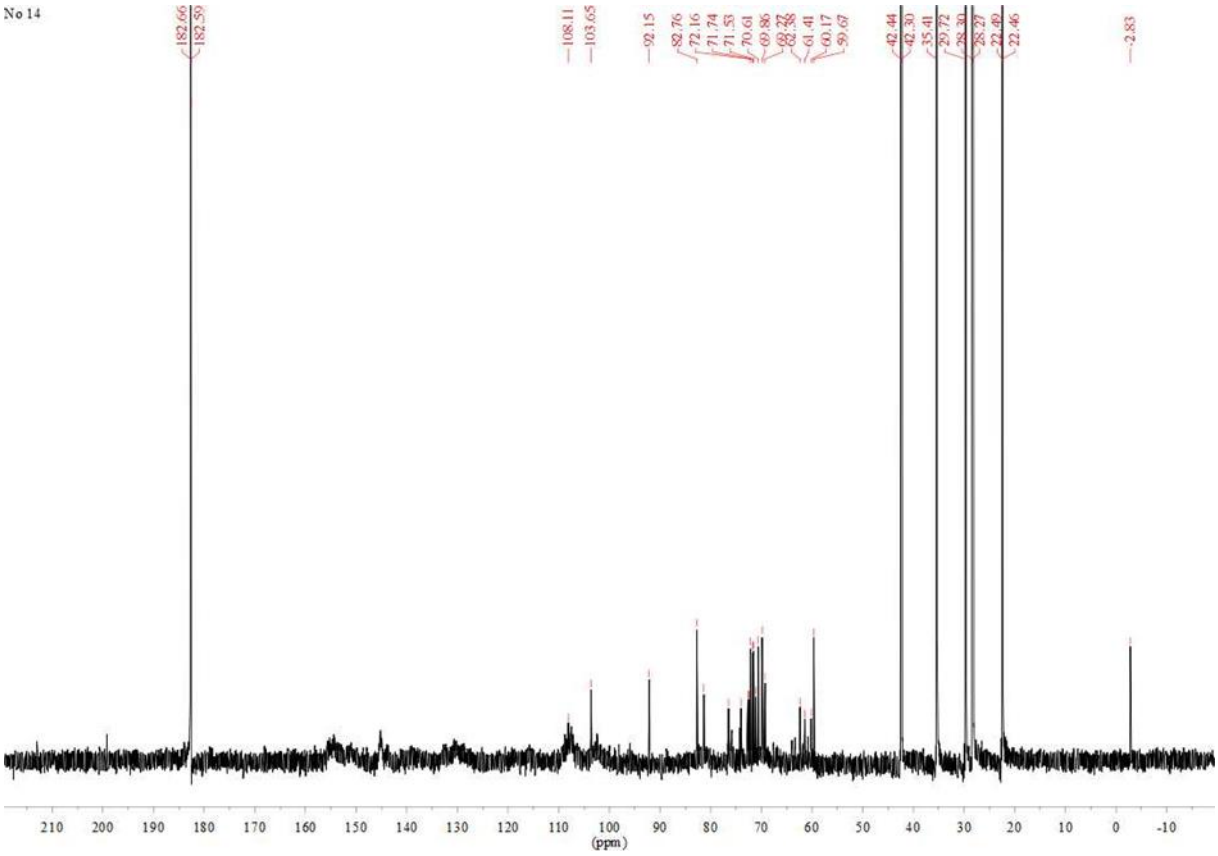

No 6
192.51
183.89
183.01
182.18
99.99
78.90
73.51
72.01
71.74
65.96
64.72
62.56
53.34
51.37
48.84
46.40
45.32
41.83
38.68
37.90
37.14
36.02
30.34
29.54
28.91
28.54
27.66
27.37
27.06
26.73
26.53
25.55
25.46
23.78
22.54
20.77
8.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

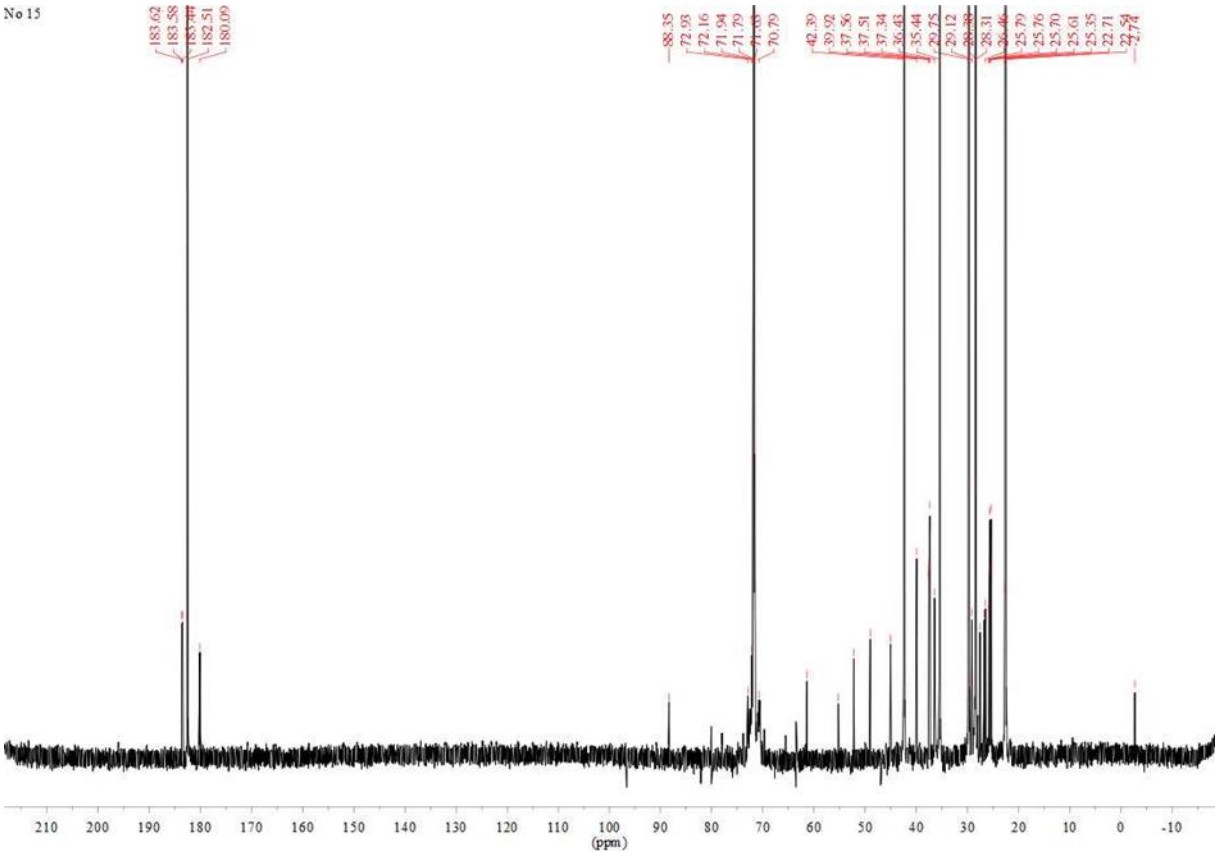

No 7
182.72
103.62
83.64
82.75
71.74
71.51
70.57
69.84
69.60
69.08
42.42
42.28
35.39
29.72
28.29
22.48
2.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

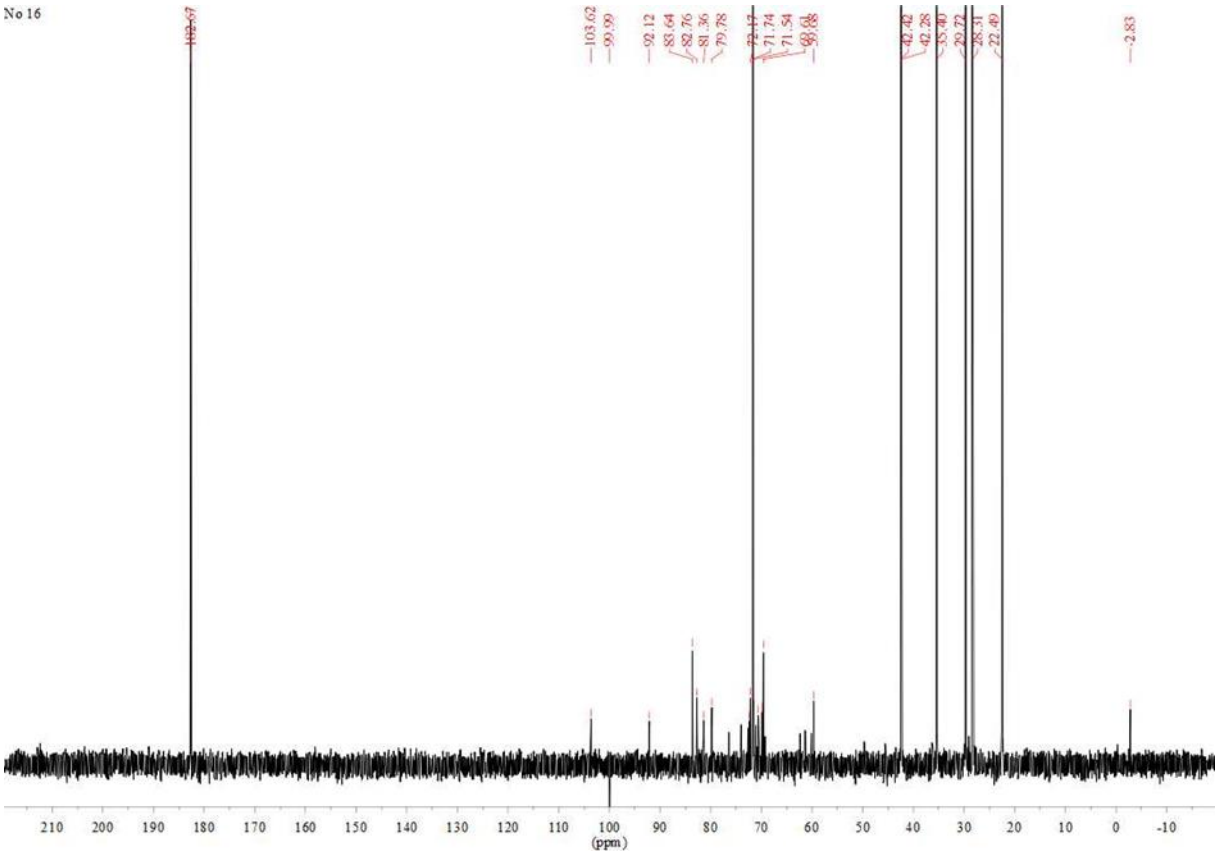

No 11
188.17
121.79
108.52
90.13
82.27
77.47
73.67
71.73
69.60
66.40
63.41
53.33
34.94
13.71
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

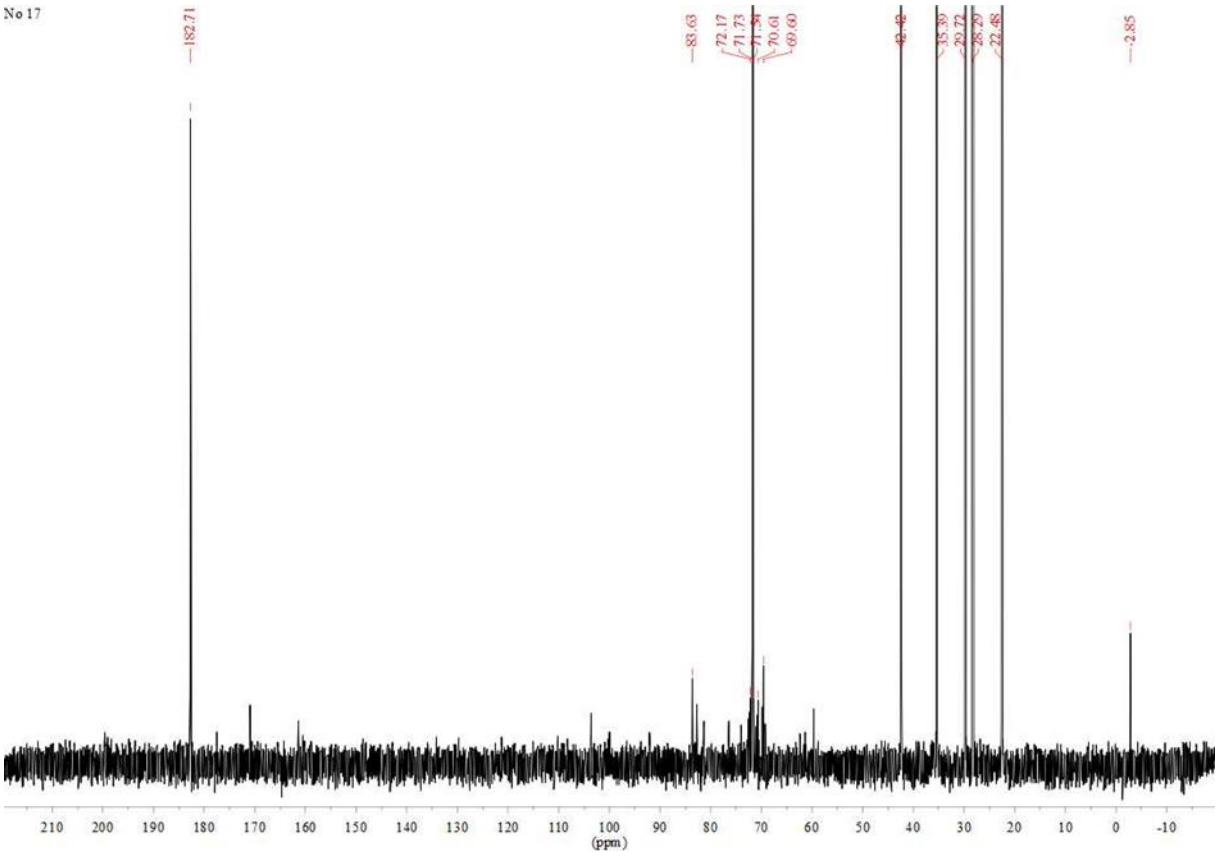

No 12
182.57
137.83
60.80
42.42
42.29
40.83
35.60
35.42
33.56
29.88
29.74
29.61
28.92
28.35
28.19
24.02
22.51
22.38
18.86
6.33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

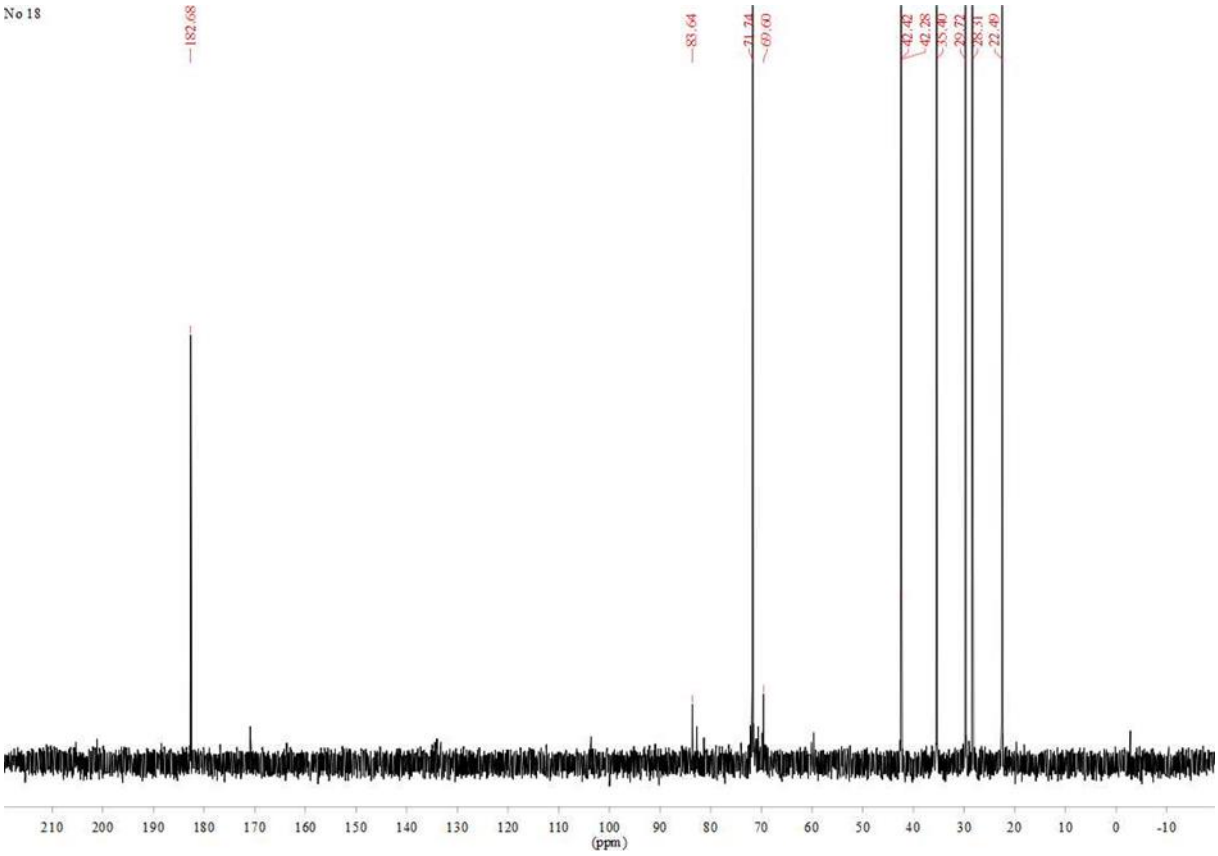

No 13
170.95
103.63
92.14
88.65
82.77
72.18
71.56
69.68
2.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


No 14
182.66
182.59
108.11
103.65
92.15
82.76
72.16
71.74
71.53
70.61
69.86
68.38
61.41
60.17
59.67
42.44
42.30
35.41
29.72
28.30
28.27
22.49
22.46
2.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


No 15
183.62
183.58
182.51
180.09
88.35
72.93
72.16
71.94
71.79
70.79
42.39
39.92
37.56
37.51
37.34
36.48
35.44
29.75
29.12
28.31
25.79
25.76
25.70
25.61
25.35
22.71
2.74
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


No 16
182.67
103.62
99.99
92.12
83.64
82.76
81.36
79.78
72.17
71.74
71.54
69.61
69.08
42.42
42.28
35.40
29.22
28.31
22.40
2.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


No 17
182.71
83.63
72.17
71.73
71.54
70.61
69.60
42.48
35.39
29.72
28.29
22.48
2.85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


No 18
182.68
83.64
71.24
69.60
42.42
42.28
35.40
29.22
28.31
22.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

Annex E. Moisture and mass losses in the specimens treated with different tannin-boron formulation exposed to brown-rot fungus *Antrodia spp*.

Formulation		Moisture content of treated samples at the end of the test (%)	Average mass loss of treated samples (%)	Moisture content of control samples at the end of the test (%)	Average mass loss of control samples (%)
Free BA	No leaching	54.96 (6.53)	0.31 (0.07)	54.35 (6.27)	56.82 (4.32)
	ENV 1250-2	53.78 (5.78)	37.95 (3.09)	55.89 (7.98)	53.88 (6.31)
	EN84	59.89 (4.01)	48.68 (2.88)	60.78 (7.66)	57.93 (5.67)
Tan. + BA	No leaching	77.20 (6.60)	1.31 (0.33)	69.80 (14.81)	55.78 (3.20)
	ENV 1250-2	54.60 (14.51)	3.35 (0.84)	70.58 (13.98)	53.78 (10.84)
	EN84	66.58 (9.87)	14.51 (3.87)	75.71 (7.89)	60.15 (3.89)
Tan. + PEG + BA	No leaching	89.78 (8.56)	1.00 (0.07)	56.13 (5.98)	57.78 (3.22)
	ENV 1250-2	69.57 (7.67)	1.63 (0.16)	57.38 (4.98)	54.87 (11.87)
	EN84	69.19 (11.79)	2.99 (0.19)	62.43 (7.68)	59.19 (4.61)
Tan. + Cap. + BA	No leaching	78.91 (6.89)	1.65 (0.25)	68.98 (7.87)	54.42 (3.76)
	ENV 1250-2	67.29 (5.38)	0.69 (0.16)	71.34 (8.86)	56.27 (9.83)
	EN84	52.65 (3.78)	0.70 (0.13)	64.68 (2.72)	60.09 (3.89)
Virulence control		Moisture content of virulent samples at the end of the test (%)		Average mass loss of virulent samples (%)	
		60.43 (0.04)		58.84 (8.90)	

Annex F. Weight losses obtained for tannin-boron-caprolactam treated wood in unsterile soils of different sites for several months

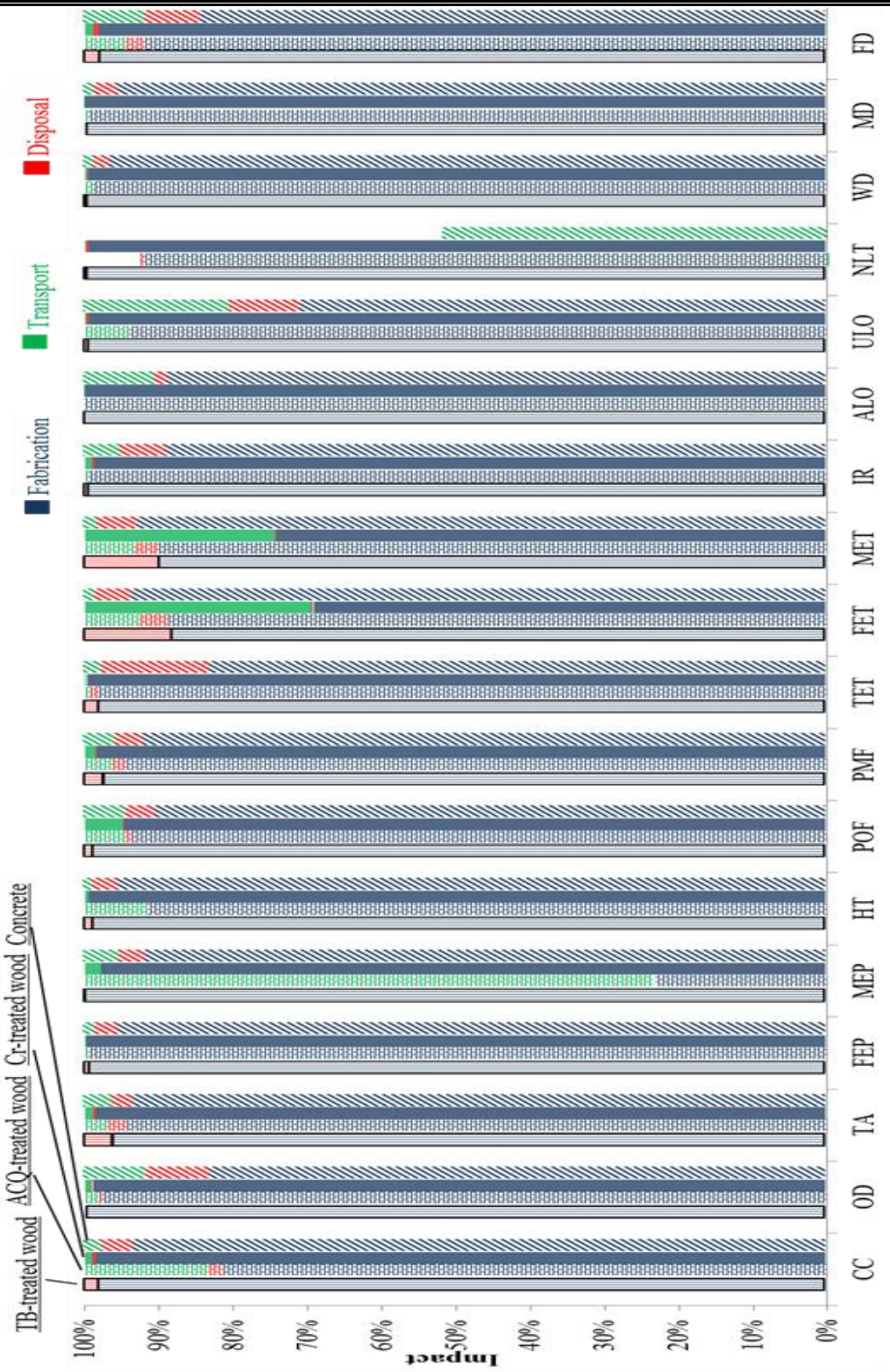
Site	Months & Species	Weight loss (%) (SD)[1]									
		0%	1%	1.5%	2%	2.5%	3%	2%(Acid)[2]	Padauk	Simarouba	Beech	Pine
Montpellier	3 P	11.99 (2.31)	9.18 (1.26)	10.61 (1.73)	11.60 (0.97)	11.44 (1.58)	11.97 (1.64)	12.05 (0.97)	0.17 (0.07)	2.91 (0.72)	35.86 (6.86)	3.40 (1.30)
	3 B	12.27 (1.62)	11.79 (0.79)	12.34 (1.21)	10.80 (1.14)	12.44 (0.95)	10.72 (0.76)	10.21 (0.70)				
	6 P	18.23 (3.41)	13.42 (2.25)	15.98 (3.39)	14.29 (1.52)	12.72 (1.02)	13.20 (0.67)	13.12 (2.01)	0.17 (0.05)	11.98 (5.92)	52.80 (10.12)	13.22 (5.40)
	6 B	20.28 (2.34)	20.45 (2.21)	16.51 (1.64)	15.24 (1.73)	17.03 (1.73)	15.81 (1.53)	13.51 (1.30)				
	10 P	23.16 (4.40)	16.78 (1.87)	16.66 (2.86)	17.73 (2.76)	17.40 (2.23)	16.21 (1.83)	16.94 (1.76)	0.29 (0.11)	14.91 (3.21)	71.77 (11.89)	17.25 (3.51)
	10 B	30.48 (1.16)	28.55 (2.96)	23.64 (2.61)	22.80 (2.27)	21.14 (1.76)	24.93 (2.22)	22.59 (3.81)				
	12 P	24.59 (3.50)	19.19 (3.55)	19.97 (3.45)	18.58 (2.28)	17.84 (2.98)	17.11 (1.88)	16.83 (1.19)	0.47 (0.06)	18.01 (6.02)	74.32 (13.44)	24.83 (3.70)
	12 B	37.72 (4.07)	35.69 (8.00)	25.56 (2.97)	25.67 (1.70)	24.27 (2.04)	28.92 (3.31)	25.90 (3.97)				
Changsha	3 P	11.23 (1.51)	9.50 (1.04)	6.47 (1.21)	6.99 (1.82)	5.90 (1.45)	6.18 (1.46)	12.40 (2.14)	0.18 (0.05)	1.66 (0.29)	12.15 (2.79)	3.27 (0.62)
	3 B	12.46 (0.67)	14.89 (3.74)	12.93 (1.30)	12.60 (1.37)	13.26 (1.62)	14.79 (1.12)	11.83 (1.39)				
	6 P	16.83 (0.88)	11.27 (0.66)	13.96 (1.75)	15.12 (1.48)	14.59 (2.52)	15.83 (1.05)	14.55 (2.15)	0.28 (0.05)	6.88 (1.89)	20.84 (4.16)	9.40 (2.10)
	6 B	22.56 (3.51)	20.67 (2.72)	20.52 (2.45)	18.69 (1.95)	19.99 (2.50)	19.53 (2.71)	17.98 (2.49)				
	10 P	18.12 (2.07)	13.15 (1.95)	14.79 (1.44)	17.84 (2.22)	17.80 (3.37)	17.73 (1.80)	15.25 (2.02)	0.34 (0.09)	7.48 (2.23)	28.58 (6.80)	10.76 (3.00)
	10 B	30.01 (2.71)	23.92 (1.99)	24.15 (1.68)	20.24 (2.15)	21.82 (1.41)	22.55 (1.57)	19.52 (2.24)				
	12 P	19.23 (1.62)	13.74 (2.92)	12.46 (1.48)	13.15 (2.12)	13.96 (1.33)	13.20 (1.95)	15.26 (1.93)	0.29 (0.09)	11.05 (2.62)	33.81 (4.21)	14.32 (3.50)
	12 B	28.39 (0.72)	24.87 (2.77)	23.15 (0.90)	21.13 (1.30)	23.35 (2.39)	21.43 (1.64)	21.71 (3.49)				

[1](SD) =standard deviation, [2](Acid) =without adding the solution of NaOH, [3]P=treated pine, [4]B-treated beech

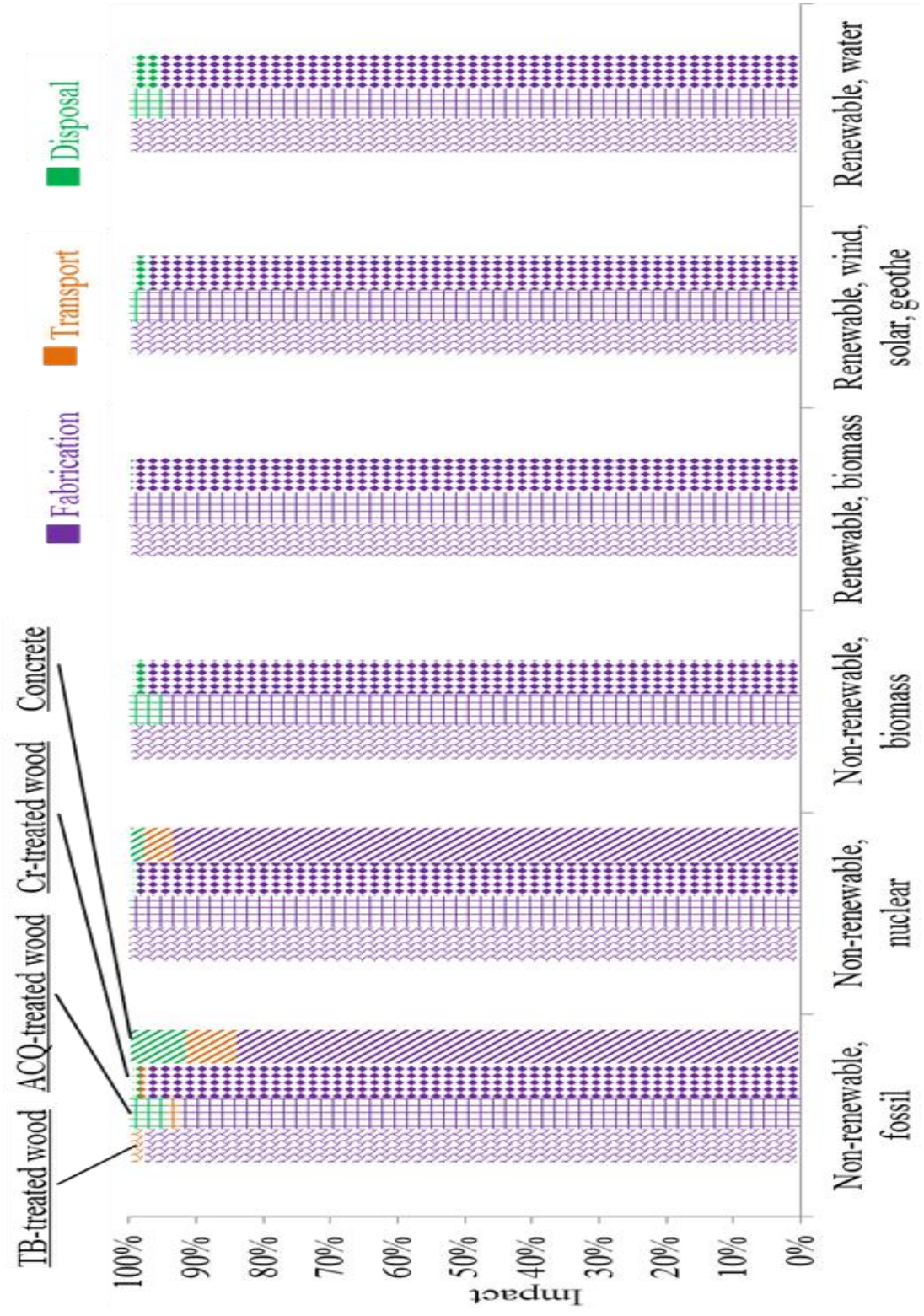
Annex G. Toxicity of boric acid in treated Scots pine and beech block exposed to selective brown and white rot in a soil jar test (Drysdale 1994)

Wood rot type	Fungus	Wood species	Minimum toxicity as boric acid	
			% w/w	Kg/m^3
Brown rot	*Lentinus lepideus*	Scots pine	0.10	0.50
	Coniophora cerebella		0.20	1.00
	Poria vaporaria		0.10	0.50
	Merulius lacrymans		<0.30	<1.60
	Poria vaillantii		<0.30	<1.60
	Lenzites trabea		<0.30	<1.60
	Trametes serialis		<0.30	<1.60
	Poria xantha		<0.30	<1.60
White rot	*Polystictus versicolor*	Beech	0.10 – 0.20	<1.00
	Polystictus ragulosus		0.25 – 0.30	1.50 – 1.60

Annex H. Comparative contributions from impact categories of ReCiPe method to each life cycle stage of per m^3 material



Annex I. Comparative contributions from impact categories of CED method to each life cycle stage of per m^3 material



Scientific products

I. Publication in press

"Advanced tannin-based wood preservatives" will be published in the Forest Products Journal (FPJ). The manuscript will appear in Volume 65, Issue 3/4 which is scheduled to mail in June 2015.

Proceedings of the 3rd International Conference on Processing Technologies for the forest and Bio-based Products Industries
24-26, September 2014, Kuchl/Salzburg, Austria

Authors: Gianluca Tondi, Jin-Bo HU, Marie-France Thevenon

II Poster of conference

"Termite resistance of the tannin-boron treated Scots pine wood after artificial and natural weathering"

Authors: Hu J.-B., Tondi G., Thevenon M.-F.

Paris, 19-21 Novembre 2013

III Poster of conference

"Fire properties of tannin-boron-montmorillonite treated wood"

Authors: Hu J.-B., Thevenon M.-F., Tondi G.

Nancy, 12-14, Novembre 2014

IV Publication in submission

In submission

"Life cycle assessment of a novel association tannin-boron for wood protection"

Authors: Jinbo HU, Campbell SKINNER, Graham ORMONDROYD, Gianluca TONDI, Antonio PIZZI, Marie-France THEVENON

V Publication in submission

In submission	*"Advanced Tannin-boron Formulation: Biological Properties"* Authors: J.B. Hu, M.F. Thevenon, S. Palanti, G. Tondi

VI Publication in submission

In submission	*"Advanced Tannin-boron Formulations Part 1: Weathering properties"* Authors: G. Tondi, J.Hu, F. Rizzo, J. Buh, S. Medved, A. Petutschnigg, M.F. Thevenon

VII STSM report

COST Action 1006 MC Chair: Dr. Stefanie Wieland (University of Stuttgart, Germany) 	*"Physical, Mechanical and Chemical Investigation of Advanced Tannin-Boron Formulations"* Author: Mr. Jinbo Hu Host institution: Salzburg University of Applied Sciences (Kuchl, Austria) Host supervisor: Dr. Gianluca Tondi Period: 25/11/2013 to 20/12/2013

VIII STSM report

COST Action 1303 MC Chair: Dr. Dennis JONES (SP Technical Research Institute of Sweden, Sweden)	*"Life Cycle Assessment of Tannin-Boron Formulations in Comparison with Commercial Preservatives"* Author: Mr. Jinbo Hu Host institution: Bangor University (Bangor, UK) Host supervisor: Dr. Graham ORMONDROYD, Mr. Campbell SKINNER Period: 06/05/2014 to 05/06/2014